PRESENCE, FATE, AND BEHAVIOUR OF EMERGING MICROPOLLUTANTS IN THE NEW ZEALAND AND ANTARCTIC COASTAL ENVIRONMENT

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For Mum & Dad

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Abstract

Many chemicals used in everyday personal care products are today amongst the most commonly detected compounds in surface waters throughout the world. Collectively referred to as micropollutants, they include paraben preservatives, organic UV filters, alkylphenols, triclosan, and bisphenol-A. Micropollutants enter the aquatic environment predominantly via wastewater discharges. To date there has been only limited assessments on their presence and impacts in coastal environments.

The wastewater treatment plants in Lyttelton, Governors Bay, and Diamond Harbour were found to discharge micropollutants into Whakaraupo Harbour. Similarly, the sewage effluents of the Antarctic research stations Scott Base and McMurdo Station were found to discharge micropollutants into Erebus Bay. Strong seasonal changes in the Whakaraupo effluent concentrations were observed, with concentrations higher in winter than in summer. Concentrations fluctuated greatly in Scott Base, reaching concentrations higher than have been previously reported internationally. The nine most commonly detected analytes were octylphenol, 4-MBC, BP-3, BP-1, triclosan, methyl triclosan, bisphenol-A, estrone, and coprostanol.

The marine environments in Whakaraupo Harbour and Erebus Bay were found to be similarly impacted. The most commonly detected micropollutants in seawater in Whakaraupo Harbour were mParaben, 4-MBC, BP-3, OMC, bisphenol-A, and estrone. The marine sediments in Whakaraupo Harbour accumulated mParaben, octylphenol, 4-MBC, BP-3, BP-1, bisphenol-A, OMC, estrone, and coprostanol, while mussels bioaccumulated mParaben, octylphenol, and BP-3. The same range of micropollutants were detected in seawater throughout Erebus Bay, including the reference sites. Marine biota (clams, urchins, and fish), including those from the reference site, were shown to readily bioaccumulate mParaben, pParaben, octylphenol, BP-3, E2, EE2, and coprostanol. A much larger coastal area of Antarctica and New Zealand is therefore impacted than was previously thought.

Photodegradation was identified as an important environmental degradation pathway for micropollutants. mParaben, BPA, EE2, and BP-3 are highly photo-stable, while triclosan and OP readily photodegrade. The low temperature and irradiance conditions in Antarctica were modelled to investigate their potential environmental persistence. Field measurements suggest the model may underestimate the photodegradation potential of some micropollutants.

Abbreviations

4-MBC – 4-methylbenzylidene camphor
ACN – Acetonitrile
APE – Alkylphenol ethoxylates
ASE – Accelerated solvent extraction
BP-1 – Benzophenone-1
BP-3 – Benzophenone-3
BPA – Bisphenol A
bParaben – Butyl paraben
DCM – Dichloromethane
DOM – Dissolved organic matter
d.w. – dry weight
EDCs – Endocrine disrupting chemicals
eParaben – Ethyl paraben
E1 – Estrone
E2 - 17β-estradiol
E3 – Estriol
EE2 – 17α-ethinyl estradiol
GC-MS – Gas chromatography mass spectrometry
GPC – Gel permeation chromatography
HCH – Hexachlorocylcohexane
HPLC – High pressure liquid chromatography
HRT – Hydraulic retention time
IPA – Isopropyl alcohol
LOD – Limits of Detection
LOQ – Limits of Quantification
l.w. – lipid weight
MeOH – Methanol
MQ - MilliQ
mParaben – Methyl paraben
NP – 4-*n*-nonylphenol
OMC – 2-ethylhexyl-*p*-methoxycinnamate
OP – 4-*t*-octylphenol
PBDEs – Polybrominated diphenyl ethers
PCBs – Polychlorinated biphenyls
PCPs – Personal care products
pParaben – Propyl paraben
SB – Scott Base
SPE – Solid phase extraction
UV light – Ultraviolet light
w.w. – wet weight
WWTP – Wastewater treatment plant

CHAPTER ONE

INTRODUCTION

1 Introduction

1.1 Background

A large number of chemicals added to personal care products (PCPs) are today amongst the most commonly detected compounds in surface and ground water throughout the world [1-3]. These compounds include a range of pharmaceuticals (antibiotics, steroids, etc), personal care product additives (antimicrobials, UV filters), and chemicals used in industry (plasticisers, plastic monomers), collectively referred to as micropollutants. Naturally occurring hormones excreted through faeces and urine also belong to this group [2, 3]. The term micropollutants includes newly developed compounds, compounds which have only recently been detected in the environment due to improved analytical methods, and compounds which have only recently been characterised as a contaminant [4].

These micropollutants are used in a diverse range of products, including soaps, lotions, toothpastes, sunscreens, fragrances, and moisturizers [1]. As such, wastewater effluent discharges are the main source of micropollutants into the environment [3, 5]. Micropollutants are becoming of increasing concern with respect to environmental health [6], due to the biological activity that some exhibit [6]. This sub-group, referred to as endocrine disrupting chemicals (EDCs), have been detected in both sewage effluent and surface waters at low ng L^{-1} up to low μg L^{-1} levels all over the world [2, 3, 7]. There is still limited information on their fate, behaviour, and potential impacts in the environment because historically only few PCP ingredients have been regulated or inventoried worldwide [2]. Environmental effects are now emerging because these compounds were not previously tested for biological activity [2, 3].

Conventional sewage treatment methods cannot completely remove micropollutants from wastewater before the effluent is released into the environment [8, 9]. Micropollutants have been shown to be able to contribute more to water toxicity than priority pollutants [10]. Priority pollutants, such as biocides and polyaromatic hydrocarbons which present a significant risk to the aquatic environment, will soon be subject to legislative control currently being discussed in the European Commission [11]. However it is important to note that this is not the complete picture. While the focus over the last three decades has been on these priority pollutants, a wide range of other, unregulated micropollutants from pharmaceuticals and PCPs may also pose a risk to humans and the environment [3]. This is in part because, while priority pollutants pose a risk due to their environmental persistence, micropollutants are continuously released into the environment and therefore do not need to be persistent to have an adverse effect [10]. This is referred to as pseudo-persistence. An increased awareness

of the risks associated with the exposure to environmental contaminants has led many regulators questioning whether our current treatment systems are still adequate enough to provide sufficient protection to aquatic environments [12]. Improved analytical technology gives us the ability to detect contaminants at ng L^{-1} levels, and has lead to the realization that a wide range of these anthropogenic compounds are reaching our surface and drinking water [2, 12].

1.2 Endocrine System and Endocrine Disruption

1.2.1 Endocrine System

Chemical regulators control every aspect of multi-cellular life, from early development and the differentiation of tissues and organs, through to reproduction [13]. Hormones play a key role in the endocrine system, and are critical in the maintenance of homeostasis. Both vertebrates as well as invertebrates (e.g. insects, molluscs, sea stars, etc) use hormones to control and regulate their development, growth, maturation, and reproduction [13]. Traditionally the endocrine system was thought to consist of a series of glands which secreted their products directly into the blood stream. However, in more recent years the neural, immune, adipose, heart, liver, and kidney cells have also been found to release chemical regulators into the blood [13]. Once in the blood stream, these regulators are transported to target cells where they bind to a specific receptor within the cell (e.g. steroid and thyroid hormones) or on its surface wall (e.g. peptides and proteins). Each hormone has a high affinity and specificity for a particular receptor, and this initiates, enhances, or inhibits specific biochemical events in the target cell [13].

1.2.2 Endocrine Disruption

The Environmental Protection Agency (EPA) defines an environmental endocrine disruptor as "an exogenous agent that interferes with the production, release, transport, metabolism, binding, action or elimination of natural hormones in the body responsible for the maintenance of homeostasis and the regulation of developmental processes" [14]. A wide range of chemicals have been identified as endocrine disruptors, including pesticides (e.g. *o,p*'-DDT, dieldrin), herbicides (e.g. atrazine), fungicides (e.g. tributyltin), industrial chemicals (e.g. polychlorinated biphenyls (PCBs)), pharmaceuticals (e.g. diethylstilbestrol), heavy metals (e.g. cadmium), products associated with plastic (e.g. bisphenol A, phthalates), and household products (e.g. alkylphenols) [15]. These chemicals can exert their effect via several different mechanisms, including [15]:

(i) inducing a normal hormone response;

(ii) causing an abnormal response or eliciting no response as it blocks the receptor site and prevents natural hormones from binding;
(iii) binding to other receptors and create a novel reaction or interfere indirectly with normal hormonal action; or
(iv) altering production and breakdown of hormone receptors and natural hormones modifying the endocrine response.

Activity via these mechanisms can cause a wide range of physiological effects in the affected organism, including infertility, sexual underdevelopment, birth defects, altered or reduced sexual behaviour, or altered thyroid or adrenal cortical function [16]. Since endocrine disruption can occur through several mechanisms this explains why a wide range of structurally dissimilar chemicals can be endocrine disrupting [15]. As such, EDCs can generally not be identified by their structure alone [15]. However, micropollutants with structural characteristics similar to steroid hormones (electrophilic functional groups such as hydroxyl groups separated by a hydrophobic region) can be used to identify some estrogenic compounds [17, 18].

A major concern is the profound and permanent effects EDCs can have if offspring are exposed during critical periods of development [19]. Some effects such as birth defects become visible during embryonic development or at birth, while other effects such as altered mating behaviour only become apparent during adulthood [19]. While the exposure of EDCs during adulthood is generally thought to not induce permanent changes in hormone-responsive tissue, some permanent changes in the brain and sexual organs have been observed in mammals [19]. Other effects observed in wildlife include effects on the reproductive organs of fish living in waterways receiving wastewater discharges, imposex marine snails caused by the anti-fouling agent tributyltin, reduced reproductive and immune functions in seals caused by PCBs, and distorted sex organ development in alligators in Florida caused by pesticides [20].

To date, the disruption of the estrogen receptor (ER) is the most studied endocrine disruption mechanism. EDCs tend to bind only weakly to the ER compared to the natural and synthetic steroid hormones, and illicit a much weaker response (Table 1.1). However, some of these less potent EDCs tend to occur in the environment at much higher concentrations than the more potent steroid hormones. The industrial chemicals nonylphenol and BPA have been detected in surface waters between sub – low $\mu g\ L^{-1}$ [21, 22], whereas the steroid hormones are present only at low $ng\ L^{-1}$ levels [21, 23]. While the concentrations of most EDCs in the aqeuous environment are below those required to cause observable physiological effects, small effects could theoretically accumulate over time until cumulative level of these effects

finally cascade to irreversible change [3]. Most estrogenic studies have been conducted under controlled conditions, and the effects of EDCs in the environment are not well understood [2]. This is especially true for the case of mixtures of EDCs [2], which is how they are present in the environment.

In recent years environmentally relevant chemicals have also been investigated for their thryoid-disrupting properties [24]. Thyroid hormones regulate metabolism, bone development, cardiac function, and physiological wellbeing [24]. In particular studies on the persistent PCBs, flame retardants such as the polybrominated diphenyl ethers (PBDEs), and pesticides have shown strong evidence for disruption of thyroid homeostasis [24]. PCPs such as BPA, the UV filters 4-MBC, BP-2, BP-3, and OMC, and the antimicrobial compound triclosan have also been shown to posses potential thyroid disrupting properties [24-26]. However their modes of action on thyroid function are still unclear and require further study [27, 28].

Table 1.1: Micropollutants and their binding affinity to the estrogen receptor (ER) and their estrogenic potency relative to 17β-estradiol.

Compound	Chemical Class/ Use	Relative ER binding affinity [a] [29-31]	Estrogenic potency relative to E2 using E-Screen [b]	Reference
17β-estradiol	Natural hormone	1	1	
17α-ethinyl estradiol	Synthetic hormone	1.2 – 8.7	1.07 – 2.2	[29, 31, 32]
Diethylstilbestrol	Synthetic hormone	1.3 – 4.7	0.83 – 2.5	[29, 32]
Estrone	Natural hormone	0.007 – 0.60	0.01 – 0.3	[29, 31, 32]
Estriol	Natural hormone	0.03 – 0.75	0.071	[29]
Bisphenol A	Plastic monomer	0.00023 – 0.0023	0.000013 – 0.00011	[2, 29, 31, 32]
4-*n*-nonylphenol	Industrial chemical	0.00018 – 0.00007	0.01 – 0.000013	[2, 29, 31-33]
4-*t*-octylphenol	Industrial chemical	0.0003 – 0.0019	0.0001 – 0.00093	[29, 31-33]
Methyl paraben	Preservative	N/A	3.3×10^{-7} – 5.0×10^{-7}	[34, 35]
Ethyl paraben	Preservative	N/A	2.0×10^{-6} – 5.0×10^{-7}	[34, 35]
Propyl paraben	Preservative	N/A	3.3×10^{-5} – 8.0×10^{-6}	[34, 35]
Butyl paraben	Preservative	N/A	0.00004 – 0.000125	[34, 35]
Benzyl paraben	Preservative	N/A	0.00002 – 0.00025	[34, 35]
Benzophenone-1	UV-filter	N/A	0.0002	[36]
Benzophenone-3	UV-filter	N/A	0.000022	[36]

[a]ER binding affinity relative to 17β-estradiol, unitless.
[b]Ratio of the EC50 of the compound divided by the EC50 of E2, except for BP-1 and BP-3, which was a yeast hERα transactivity assay.

1.3 Sources and Concentrations of Micropollutants in the Environment

Micropollutants are known to be environmentally unstable (or labile) as a result of photo-degradation and hydrolysis [2]. The majority of micropollutants are hydrophilic and have a

low K_{OW} [2]. Losses such as binding to organic fractions of sludge and suspended sediments are therefore low compared to other persistent organic compounds such as PAHs, PCBs, and organochlorine pesticides [2]. However, micropollutants are continuously released into the environment and therefore do not need to remain stable for extrended periods of time to have adverse effects [10].

1.3.1 Sewage as a Source of Micropollutants

The main inputs of micropollutants into the environment are industrial and household sewage [3, 5, 6]. As PCPs are mainly designed for external use on the human body, many micropollutants are not subjected to metabolic alterations [5], and can wash directly off the skin in the shower or during recreational activities [37, 38]. Hence large quantities of micropollutants can reach the environment unchanged, even after wastewater treatment [1, 8, 9], and in some instances may completely avoid the water treatment processes [37-39]. Micropollutants can also enter the human body via dermal absorption after the application of sunscreens [40, 41], or the use of oral care products [42]. Food packaging has also been identified as a possible route of exposure [43]. These micropollutants are then excreted from the body via the urine and faeces [44]. The amount of micropollutants reaching a wastewater treatment plant (WWTP) largely depends on the size of the human population serviced, the quantity and duration of PCP consumption, and how quickly these are excreted from the body [2]. It is unknown whether age distribution and life style choices also play a role [2].

Because of the high but variable removal efficiency of current WWTPs (Section 1.3.2) the concentration ranges of micropollutants in the influent and effluent can overlap quite considerably for some compounds (Table 1.2). The effluent concentrations are of most environmental concern, and can reach a maximum of low μg L^{-1} concentrations for most compounds. However concentrations in the medium ng L^{-1} range are most commonly found.

Table 1.2: Internationally reported range of concentrations of micropollutants in the influent and effluent of domestic WWTPs.

Compound	Chemical Class/Use	Matrix	Range (ng L^{-1})	Reference
Methyl paraben	Preservative	Influent	12.5 – 9,880	[45-47]
		Effluent	2.1 – 423	[47-49]
Ethyl paraben	Preservative	Influent	2.2 – 719	[46, 47]
		Effluent	<0.3 – 69	[47, 49, 50]
Propyl paraben	Preservative	Influent	43 – 2,640	[47, 51, 52]
		Effluent	<0.25 – 95	[47, 49, 53]
Butyl paraben	Preservative	Influent	9.7 – 864	[47, 51, 52]
		Effluent	<0.2 – 83	[46, 47, 50, 51]
4-*t*-octylphenol	Industrial chemical	Influent	<1.2 – 4,500	[47, 51, 54]
		Effluent	<1.2 – 3,949	[47, 49, 51]
4-*n*-nonylphenol	Industrial chemical	Influent	70 – 25,000	[47, 51, 54]
		Effluent	<29 – 3,210	[47, 51, 54]

4-methoxybenzylidene camphor	UV-filter	Influent	278 – 6,500	[55-57]
		Effluent	42 – 2300	[56, 58]
Benzophenone-3	UV-filter	Influent	11 – 7,800	[56, 59, 60]
		Effluent	3 – 2,196	[49, 55, 56]
Benzophenone-1	UV-filter	Influent	31 – 700	[49, 59, 60]
		Effluent	<2 – 41	[49, 59, 61]
2-ethylhexyl-*p*-methoxycinnamate	UV-filter	Influent	54 – 19,000	[55-57]
		Effluent	<10 – 177	[56-58]
Triclosan	Antimicrobial	Influent	52 – 86,200	[62]
		Effluent	10 – 5,370	[62]
Methyl triclosan	Metabolite	Influent	<1 – 307	[63, 64]
		Effluent	<2 – 51	[63, 64]
Bisphenol-A	Plastic monomer	Influent	80 – 4980	[22]
		Effluent	6 – 3642	[22]
17α-ethinyl estradiol	Synthetic hormone	Influent	<0.2 – 70	[65]
		Effluent	<0.3 – 7.5	[65]
Estrone	Natural hormone	Influent	<10 – 670	[66]
		Effluent	<0.1 – 147	[66, 67]
17β-estradiol	Natural hormone	Influent	2.4 – 161.6	[66]
		Effluent	0.2 – 158	[66]
Estriol	Natural hormone	Influent	10 – 660	[66]
		Effluent	0.43 – 275	[66]

1.3.2 Sewage Treatment Efficiency

A wide range of systems are available for the treatment of wastewater, however activated sludge treatment remains the workhorse technology [2]. Indeed this system can achieve removal efficiencies of well over 90% for micropollutants [2, 68, 69]. However removal efficiencies are variable and can be reduced significantly [68]. These depend largely on the age of the activated sludge, the season of the year (i.e. temperature and sunlight intensity), and the hydraulic retention time (HRT) of the WWTP [2, 68]. The physiochemical properties of the chemical also play an important part in its removal, which can make it difficult to select a treatment method capable of removing all classes of contaminants [2]. Sunlight enhances the photodegradation of some micropollutants, while increased temperatures and extended HRTs support biodegradation [2]. High removal efficiencies can also be obtained using advanced processes such as membrane bioreactors, activated carbon, membrane filtration, advanced oxidation processes (e.g. photocatalysis with TiO_2 and/or H_2O_2), and ozone disinfection [2, 68]. However these processes are expensive and their use is often not practical or feasible [68]. The optimization of the operational parameters of the conventional activated sludge treatment is therefore the best option to achieve high and consistent removal efficiency without increasing operational costs [68]. This is currently an area of intense research [68].

1.3.3 Micropollutants in the Aquatic Environment

To date the majority of research on micropollutants has focused on freshwater environments such as rivers and lakes. The presence of micropollutants in marine environments such as harbours, lagoons, estuaries, and bays has received only limited attention, especially for micropollutants such as the paraben preservatives [50], UV filters [38, 39, 70, 71], and triclosan [72-74]. Micropollutants such as bisphenol-A, octylphenol, and nonylphenol have been studied more frequently due to their industrial relevance. Concentrations are generally lower in marine environments than rivers and lakes (Table 1.3). This is likely to be due to the higher dilution potential of the ocean. Heavily polluted rivers can contain micropollutant concentrations up to the low μg L^{-1} range. However this is the case primarily for heavily used compounds such as methyl paraben, nonylphenol, triclosan, and bisphenol A (Table 1.3). Micropollutant concentrations generally lie in the low to medium ng L^{-1} range.

Table 1.3: Internationally reported concentrations of micropollutants in freshwater and seawater.

Compound	Chemical Class/Use	Matrix	Range (ng L^{-1})	Reference
Methyl paraben	Preservative	River water	<0.3 – 1,062	[21, 47, 49]
		Seawater	2.1 – 51	[50]
Ethyl paraben	Preservative	River water	<0.3 – 147	[47, 49, 75]
		Seawater	<0.3 – 6.7	[50]
Propyl paraben	Preservative	River water	<0.2 – 2,141	[21, 49, 50]
		Seawater	<0.5 – 7.9	[50]
Butyl paraben	Preservative	River water	<0.2 – 54.1	[47, 49, 50, 52]
		Seawater	<0.2 – 0.7	[50]
4-*t*-octylphenol	Industrial chemical	River water	<1.2 – 1,293	[47, 49, 76]
		Seawater	0.04 – 81	[77-79]
4-*n*-nonylphenol	Industrial chemical	River water	<10 – 33,231	[21, 80, 81]
		Seawater	1.3 – 275	[77, 79, 82]
4-methoxybenzylidene camphor	UV-filter	River water	12 – 140	[58, 83]
		Lake water	<2 – 1,140	[55, 56]
		Seawater	13.1 – 798.7	[39, 70]
Benzophenone-3	UV-filter	River water	2 – 729	[58, 76, 84, 85]
		Lake water	<2 – 125	[55, 56, 86]
		Seawater	1.8 – 3,300	[38, 70, 71]
Benzophenone-1	UV filter	River water	<0.3 – 37	[49, 60, 61]
		Seawater	280 ± 30	[71]
2-ethylhexyl-*p*-methoxycinnamate	UV filter	River water	6 – 1,040	[58, 83, 84]
		Lake water	<2 – 3,009	[55, 56, 86]
		Seawater	7.4 – 389.9	[39, 70]
Triclosan	Antimicrobial	River water	1 – 5,160	[21, 58, 75, 87]
		Lake water	1.3 – 14	[23, 63, 88]
		Seawater	0.0001 – 28.9	[72-74]
Methyl triclosan	Metabolite	River water	<0.3 – 12	[64, 89]
Bisphenol A	Plastic monomer	River water	1.9 – 8,300	[22]
		Seawater	<0.04 – 330	[22]
Ethinylestradiol	Birth control pill	River water	1 – 101.9	[21, 90]
Estrone	Natural hormone	River water	<0.1 – 103.9	[66, 90]
17β-estradiol	Natural hormone	River water	<0.3 – 20	[66, 91]
Estriol	Natural hormone	River water	0.43 – 51	[66, 67]

1.3.4 Environmental Fate of Micropollutants

Once released into the environment, organic chemicals including micropollutants are subjected to a range of interconnected physical, chemical, and biological processes which can lead to the removal or transformation of the chemical [92]. These processes can be divided into two major categories: processes which leave the chemical structure unchanged, and those which transform the chemical into one or more products. The first category includes transport and mixing processes within and between different phase, such as mixing within a body of water or sediments, sorption, sedimentation, and uptake by organisms [92]. The second

category includes chemical, photochemical, and biological (in particular microbial) transformations [92].

For this thesis the most important of the non-transformational processes is sorption of micropollutants to sediments and suspended particulates. Sorption is an important process as it can protect micropollutants from other degradation processes such as biodegradation [92, 93] and photodegradation [92, 94], and reduce the bioavailability of the compound [92]. The extent to which sorption processes in the aquatic environment occur strongly depends on the chemical structure of the pollutant [92] and the mineral and organic matter content of the sediments or suspended matter [92, 93]. Chemicals with charged functional groups preferentially adsorb via electrostatic interactions to oppositely charged surfaces such as mineral surfaces [92]. Neutral chemicals, such as those studied in this thesis, preferentially adsorb onto sediments and suspended particulates with neutral hydrophobic surfaces, which becomes energetically more favourable with increasing amounts of organic carbon [92]. The exception to this is triclosan, which with a pKa of 8.1 [95] is present in an anionic form between 40 – 50% of total triclosan at a seawater pH of ~8. The environmental relevance of this is discussed in more detail in Chapter Five. The sorption ability to organic carbon is expressed with the soil-water partitioning coefficient normalized to organic carbon, K_{OC} [92]. The sorption ability of micropollutants is also expressed with the *n*-octanol/water partitioning coefficient K_{OW} [96]. Compounds with a high molecular weight and a log $K_{OW} > 5$ are thought to easily absorb to sediments [96], and persistent organic pollutants are defined as chemicals with log $K_{OW} > 5$ [96].

Micropollutants may also accumulate in biota (Section 1.4). For aquatic biota the key bioaccumulation processes can be divided into direct partitioning between the water, sediments, and organism, and more complicated partitioning between consumed food and subsequent internal transport processes within the organism [92]. The chemical may become metabolized and/or excreted by the organism, or it may partition and accumulate within the different tissues of the organism (lipids, protein, polysaccharides, etc) [92]. Bioaccumulation is discussed in more detail in Section 4.3.5.

Chemical transformations such as hydrolysis or redox reactions [92] are likely to not play an important role in the degradation of PCP derived micropollutants as they were designed to remain stable in the presence of water. The transformational processes most relevant to this thesis are microbial and photochemical. Microbial processes are particularly important during wastewater treatment. Many micropollutants from personal care products contain hydroxyl functional groups, which can become conjugated (glucuronidates, sulfates, acetylates, or amino) prior to excretion from the body [3]. During wastewater treatment these conjugates are

cleaved by microorganisms [3]. Many micropollutants are then further degraded as discussed in Section 1.3.2. Microbes are strongly influenced by the composition of the microbial community, the environmental conditions (temperature, pH, salinity, oxygen, and nutrients), and the structural features of the chemical [92]. Lastly, photochemical transformation mediated by sunshine is thought to be the most important abiotic degradation process determining the fate of organic chemicals in surface waters [97], and is discussed in more detail in Chapter 5.

The micropollutants transformation products themselves can in some instances also become environmentally relevant due to enhanced toxicity and/or persistence. However, in many cases these transformation products, their toxicities, and environmental persistence are unknown. The UV-filter BP-3 can be degraded to BP-1 by loss of the methoxy functional group [98]. BP-1 has been shown to poses slight estrogenic properties [1]. Methyl triclosan, the microbial transformation product of triclosan, can be of concern due to its increased lipophilicity and environmental stability compared to triclosan [62, 63, 99]. In the case of the environmentally relevant and biologically active alkylphenols nonylphenol and octylphenol [100] their origin is the biodegradation of the commonly used industrial alkylphenol ethoxylates (APEs).

1.4 Target Analytes

Target analytes were selected based on their usage as PCP ingredients, and on their reporting frequency in the literature. They represent a range of different classes of personal care product additives and/or active ingredients, namely paraben preservatives, UV filters, antimicrobials, surfactants, and industrial use chemicals. Their specific application and known environmental behaviour is reviewed below. All chemical structures and key physical characteristics are provided in Table 1.4.

1.4.1 Organic UV Filters

Sunscreen products have been in use for approximately 80 years, and are applied externally to absorb UV radiation detrimental to human skin [40]. They are also incorporated into textiles, plastics, optical products, and agricultural chemicals to protect against UV-irradiation [83]. The growing public concern over the harmful effects of UV radiation has lead to an increased consumption of UV filters [1]. UV filters can comprise greater than 10% of the product by mass, and are usually a mix of three to eight different compounds [101]. In the US there are currently 16 UV filters certified for use in sunscreen products, and 27 UV filters certified for use in cosmetics and plastics [1]. Despite their high usage, there is still relatively little known about their environmental concentrations [1]. The main inputs of UV filters in the environment are either indirectly via WWTPs [55, 58, 59] or directly from washing off the

skin during recreational activities such as swimming [37-39]. In summer, the latter source can lead to UV filter concentrations in localized bodies of water with low flush rate, such as lakes, fjords, and beaches becoming as high as in some sewage effluent [39, 71]. They have even been detected at trace levels in the microsurface layer of the Central Pacific region [102].

The potential of organic UV filters to accumulate in the aquatic and biological environment [3, 56, 103] and inducing a physiological response [104-106] has recently become of concern. UV filters can bioaccumulate in aquatic organisms due to their high lipophilicity [1] and relative stability in the environment [97]. They can bioaccumulate in fish at levels similar to PCBs and DDT [3], and have been detected in a range of invertebrates, fish, and birds, in particular BP-3 and OMC, at up to mid ng g^{-1} levels [56, 83]. It has been proposed that OMC biomagnifies along specific prey-predator routes, providing bioconcentration factors (BCFs) ranging between 167 – 1,500 [83]. Similarly, lipid based BCFs between 9,700 – 23,000 have been reported for 4-MBC [56]. There is now concern over the presence of UV filters in the aqueous environment [105] due to the hormonal activity that many have been shown to posses [107]. Most UV filters have been shown to exhibit estrogenic activity [1, 105, 107], but antiestrogenic, androgenic, and antiandrogenic activity have also been reported [1]. BP-3 and BP-1 have been shown to affect the growth of fish (LOEC = 3,900 μg L^{-1} and 4,919 μg L^{-1} respectively) and induce vitellogenin production (LOEC = 620 – 749 μg L^{-1} and 4,919 μg L^{-1} respectively) [1]. 4-MBC and OMC have also been shown to induce vitellogenin production (LOEC = 9,900 μg L^{-1} and 9,870 μg L^{-1} respectively) [108]. BP-3 has been shown to adversely affect the fecundity of Medaka (*Oryzias latpides*), and vitellogenin production was observed at exposure levels of 620 – 749 μg g^{-1} [109]. Toxic effects of BP-3 and BP-1 have also been observed for the crustaceans *Daphnia magna* and *Acartia tonsa* [109]. Based on a preliminary environmental risk assessments the UV filters 4-MBC and OMC are of most environmental concern [109, 110].

The UV filters 4-methylbenzilidine-camphor (4-MBC), benzophenone-3 (BP-3), 2-ethylhexyl-*p*-methoxycinnamate (OMC), and benzophenone-1 (BP-1), which is a metabolite of BP-3 [98] were selected for this study.

1.4.2 Preservatives

Parabens are primarily used as antimicrobial agents in cosmetics, toiletries, pharmaceuticals, and foodstuffs [1]. The antimicrobial potency of parabens increases with increasing alkyl chain length, complementing a decrease in water solubility [34, 111]. For this reason a mixture of parabens are combined into products to ensure optimal antimicrobial activity. Methyl paraben (mParaben) and propyl paraben (pParaben) are predominantly used [1, 111]. Parabens have been shown to poses estrogenic activity [108, 112], which increases with

increasing length of the alkyl chain [34]. bParaben showed the most competitive binding to the rat estrogen receptor of the methyl – butyl paraben range [112], with a yeast estrogen screen activity of 10^{-6} M [112]. However, in *in vivo* assays only butyl-, isobutyl-, and benzylparaben were shown to be estrogenic [34]. Parabens have been shown to have a negative effect on sperm counts in animals, however these effects did not occur at environmentally relevant levels [34]. Two laboratory based high-concentration fish exposure studies have demonstrated the bioaccumulation potential of mParaben [113] and pParaben [114].

mParaben, ethyl paraben (eParaben), and pParaben readily biodegrade under aerobic conditions [111], and bParaben can readily photodegrade [115]. The log octanol/water coefficients (log K_{OW}) are relatively low, and range from 1.66 for mParaben to 3.24 for butyl paraben (bParaben) [34].

For this study mParaben, eParaben, pParaben, and bParaben have been selected.

1.4.3 Triclosan

Triclosan is an antimicrobial agent used in soaps, deodorants, lotions, toothpastes, and textiles [62], and is often added as a slow release chemical to plastics such as children toys and chopping boards [3]. Triclosan is one of the most commonly detected organic wastewater compounds, and has been detected in surface waters worldwide [62]. It can readily photodegrade, and pH and salinity strongly influence its degradation [62]. In its dissociated form (pK_a = 8.1) at basic pH it has been shown to photodegrade 19 times faster than the undissociated form [116]. Triclosan can also be biotransformed to the more lipophilic methyl triclosan (mTriclosan) during wastewater treatment [62, 99]. This compound is of greater environmental concern due to its resistance to photodegradation [62, 63, 99], and its higher potential to bioaccumulate [62]. Its bioaccumulation has been correlated to the population size of the wastewater treatment plant (WWTP), and has been proposed as a good WWTP indicator [99].

Triclosan has been shown to accumulate in a number of trophic species, including algae [117], snails [117], fish [117, 118], and dolphins [73]. Similarly, bioaccumulation of mTriclosan was observed in algae [117], snails [117], and fish [63, 99, 117, 119]. A wide variety of aquatic organisms, including algae, microorganisms, amphibians, and fish larvae are sensitive towards triclosan toxicity [62]. Triclosan can affect the swimming performance of fish, and has been shown to be slightly estrogenic [1]. Algae and microorganisms are particularly sensitive, with observable effects on algal growth occurring below 1 μg L^{-1} [1]. The bioaccumulation of triclosan through algae [117], and its high toxicity towards this important

component of the aquatic food chain is of particular concern [62]. Chronic risks due to bioaccumulation have been proposed to be more important than acute impacts, with algal species having higher bioconcentration factors than higher trophic species such as snails and fish [62]. Due to this toxicity whole ecosystems can potentially be disturbed [62].

1.4.4 Octylphenol and Nonylphenol

Octylphenol (4-*t*-octylphenol, OP) and nonylphenol (4-*n*-nonylphenol, NP) are biodegradation products of alkylphenol ethoxylates (APE), which are predominantly used as non-ionic surfactants and antioxidants [120, 121]. They are used in the production of paper, textiles, emulsifiers, paints, and personal care products [120], as well as intermediates in the production of phenolic resins [120]. Approximately 80% of all APEs produced worldwide are nonylphenol ethoxylates, with the remaining 20% being octylphenol ethoxylates [100]. Because of their widespread use they are commonly detected in wastewater, surface waters, and biota worldwide [120]. Octylphenol and nonylphenol have a low water solubility (12.6 mg L^{-1} and 5.4 mg L^{-1} at 20.5°C respectively [122]), and are therefore likely to bioaccumulate [100]. While alkylphenols can be readily metabolized in fish they have nonetheless been shown to bioaccumulate [100]. There is increasing concern about their wide usage because of their relative stability in the environment and the endocrine disrupting effects they can cause in marine and freshwater species [100]. Their estrogenicty has been demonstrated in both *in vitro* and *in vivo* studies [100]. Both OP and NP have been shown to induce the production of vitellogenin in male fish [100], and OP has been shown to inhibit testicular growth in rainbow trout [123]. Octylphenol can also decrease the growth of the cyanobacteria *Microcystis aeruginosa* at low μg L^{-1} concentrations [124].

1.4.5 Bisphenol-A

Bisphenol-A (BPA) is a high production volume chemical. Up to 95% of the produced volume is used in the production of polycarbonate plastics and epoxy resins [22] used in a variety of products such as food can and drinking water pipe linings, and automotive and electrical equipment [22]. Due to the wide usage of BPA-containing products it is now commonly detected in river and coastal waters worldwide [22, 125]. While the leaching of BPA from products can be an environmental source [22, 126], the main environmental inputs are domestic and industrial sewage effluent and landfill sites [22, 126]. The increasing release of BPA is a cause for concern as this increased exposure will result in an increase of endocrine disruptive effects that BPA is known to facilitate [126].

Bacteria, plankton, and plants have been shown to be able to remove BPA from the aquatic environment [126], but is more resistant to biological degradation in seawater compared to

freshwater [127]. Photodegradation has also been shown to assist in the breakdown of BPA in surface waters, but can be a slow process if insufficient dissolved organic matter is present [128].

A wide range of studies have shown the endocrine disruptive effects of BPA on fish, amphibians, and aquatic invertebrates even at low μg L^{-1} concentrations [126]. One of the most sensitive organisms was the midge *Chironomus riparius,* which showed developmental effects at an exposure level of only 78 ng L^{-1} [129]. BPA has been shown to bioaccumulate in fish exposed to wastewater effluent [130], and has been detected in a wide range of seafood including shellfish, squid, and fish [131].

1.4.6 Steroid Hormones

Steroid hormones are biologically active compounds produced and excreted by humans and animals [67]. Domestic and livestock waste are therefore the main sources of steroid hormones to the environment [67]. Due to their strong biological activity only small amounts of steroid hormones (low ng L^{-1}) are required in the aquatic environment to cause endocrine disruption in biota [66, 132]. The exposure of EE2 to *Danio rerio* resulted in dose-dependent increases of in vitellogenin production starting at 2 ng L^{-1} [133]. Fish development also became skewed towards the female direction at an exposure level of 1 ng L^{-1}, with complete sex reversal taking place at 2 ng L^{-1} [133].

While steroid hormones are mainly excreted as inactive glucoronide or sulphate conjugates, bacteria can cleave these during the wastewater treatment process [67]. Steroid hormones can therefore be the main contributor to the estrogenicity of wastewater effluent [132]. Though steroid hormones are expected to bind strongly to sediments, they have been widely reported in surface waters and ground waters [67].

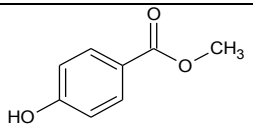
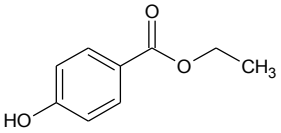
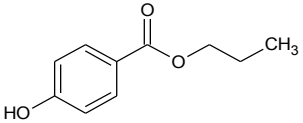
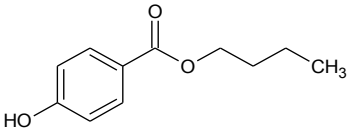
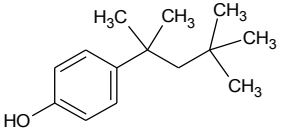
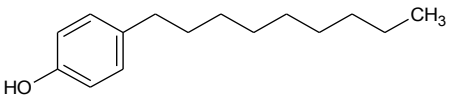
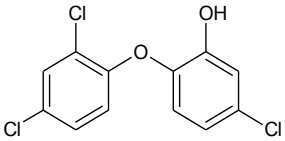
For this study the main estrogens estrone (E1), 17β-estradiol (E2), estriol (E3), and the birth control ingredient 17-α-ethinylestradiol (EE2) were selected.

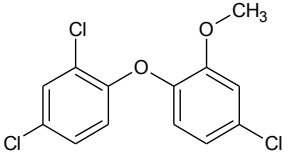
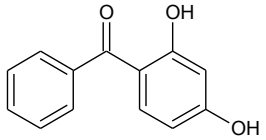
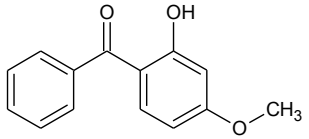
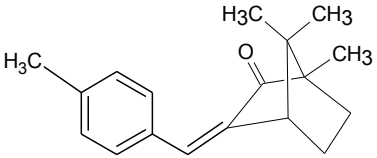
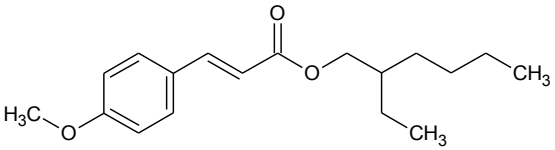
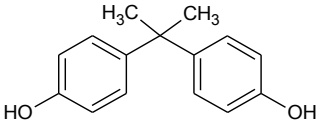
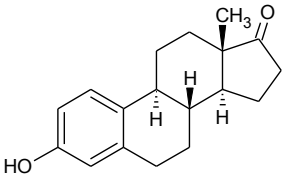
1.4.7 Faecal Steroids

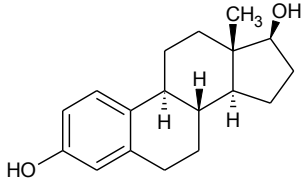
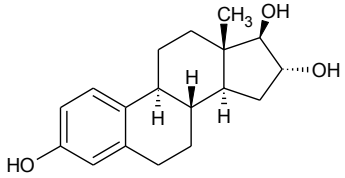
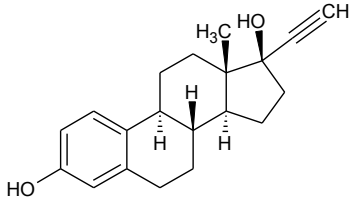
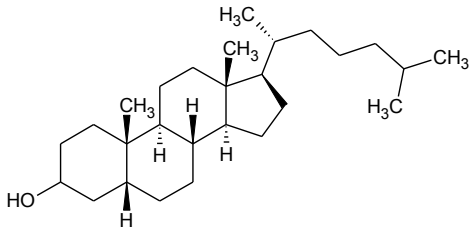
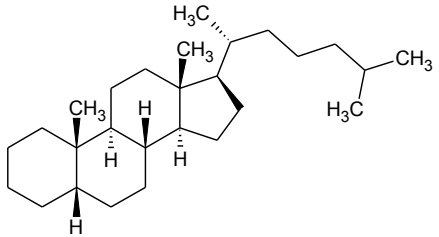
Human-derived faecal steroids have been used as tracers for sewage contamination in water and sediments for several decades [134]. Coprostanol has been widely used to date, and is formed by the biohydrogenation of cholesterol in the small intestine [134, 135]. It is only produced by higher animals, including humans. In the marine environment marine mammals are a potential natural source of coprostanol, however these contributions are likely to be minimal due to their small biomass compared to WWTPs [134]. Coprostane, the oxidation

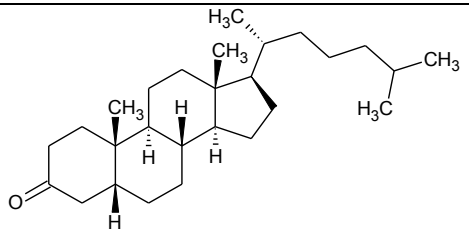
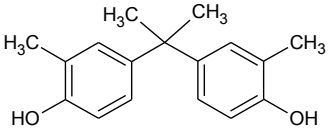
product of coprostanol, has also been used as a steroid marker [134, 135]. Coprostanol, coprostane, and coprostane-3-one have therefore been included in this study as markers

Table 1.4: List of micropollutants identified as target anlaytes for this thesis, including their main uses and key physical characteristics (obtained from Chemspider database).

Name	Structure	CAS	LogD at pH 7.4[a]	Log K_{OC}[b]	BCF at pH 7.4[c]	Application
Methyl paraben (mParaben)		99-76-3	1.83	2.35	14	Preservative (personal care products and food stuffs)
Ethyl paraben (eParaben)		120-47-8	2.34	2.63	34	Preservative (personal care products and food stuffs)
Propyl paraben (pParaben)		94-13-3	2.84	2.89	82	Preservative (personal care products and food stuffs)
Butyl paraben (bParaben)		94-26-8	3.35	3.17	200	Preservative (personal care products and food stuffs)
4-t-octylphenol (OP)		140-66-09	5.18	4.19	5,083	Surfactant, plasticiser
4-n-nonylphenol (NP)		104-40-5	6.14	4.72	27,369	Surfactant, plasticiser, spermicide
Triclosan		3380-34-5	5.20	4.14	4,850	Antibacterial agent (soaps, shampoo, sports clothing)

Methyl triclosan (mTriclosan)		4640-01-1	5.27	4.24	5,949	Triclosan metabolite
Benzophenone-1 (BP-1)		131-56-6	2.91	2.85	83	UV filter (sunscreen, cosmetics, BP-3 metabolite)
Benzophenone-3 (BP-3)		131-57-7	3.77	3.32	378	UV filter (sunscreens, cosmetics)
4 – methylbenzylidene camphor (4-MBC)		36861-47-9	3.39	3.22	220	UV-filter (sunscreens, cosmetics)
2-ethylhexyl-*p*-methoxycinnamate (OMC)		5466-77-3	5.92	4.60	18,620	UV filter (sunscreens, cosmetics)
Bisphenol A (BPA)		80-05-7	3.64	3.36	344	Polycarbonate precursor
Estrone (E1)		53-16-7	3.62	3.35	334	Natural hormone

17β-estradiol (E2)		50-28-2	4.15	3.36	832	Natural hormone
Estriol (E3)		50-27-1	2.53	2.75	49	Natural hormone
17α-ethynyl-estradiol (EE2)		57-63-6	4.11	3.61	776	Birth control pill
Coprostanol (Cstanol)		360-68-9	10.07	6.85	1,000,000	Faecal steroid (cholesterol derivative)
Coprostane (Cstane)		481-20-9	11.95	7	1,000,000	Faecal steroid

Coprostan-3-one (Cstan3one)		601-53-6	9.60	6.60	1,000,000	Faecal steroid (oxidation product of coprostanol)
Bisphenol C (IS)		79-97-0				Internal Standard

[a] Distribution coefficient of ionized plus un-ionized compound between *n*-octanol and water, i.e. pH 7.4 adjusted K_{OW} (K_{OW} also referred to as logP).

[b] Distribution coefficient of compound between the soil organic carbon and water phase.

[c] Estimated bioconcentration factor at pH 7.4.

1.5 Relevance to Antarctica

Most studies on micropollutants have been conducted in temperate climates, and their environmental fate and behaviour is currently an area of intense research. There is limited data on the fate and behaviour of micropollutants in the polar environments. Concerns have already been raised in the Arctic on the risks which the release of contaminants from untreated sewage may have on the environment. These concerns have arisen due to the low biodiversity, low ambient temperatures, and consequently the more vulnerable ecosystems [136]. To date, the majority of studies of organic contaminant pollution in the Antarctic have focused on organochlorine compounds [137-142], PAHs [143, 144], polychlorinated biphenyls (PCBs) [138-140], polybrominated diphenyl ethers (PBDEs) [141, 145-147], organophosphorus flame retardants [148], and phthalates [143, 144, 149, 150] in both seawater and wildlife. Micropollutants have not previously been identified as potential environmental pollutants in the Antarctic. Products such as sunscreens and moisturisers containing UV filters and preservatives are high use items in Antarctica due to the high UV light prevalence and dry atmosphere.

Micropollutants and other environmental pollutants are, depending on their chemical properties, subjected to a range of natural removal processes, such as sorption to sludge and sediments, calcification, microbial degradation, and photodegradation [6, 151]. The majority of available knowledge on the fate and behaviour of micropollutants has come from studies conducted at temperate environmental conditions. This knowledge may not be fully applicable to the Antarctic environment due to the permanently low temperatures, fluctuating light regimes, and unique wildlife.

1.6 Thesis Rationale and Objectives

As outlined in the previous sections, there is concern over the growing numbers of chemicals being detected in the aquatic environment worldwide. This is especially true for micropollutants, which are likely to increase in number as analytical methods improve and more research is carried out. The majority of studies on micropollutants have focused on freshwater environments such as rivers, lakes, and groundwater. There is a lack of research on the presence of micropollutants in the coastal and estuarine environments. These areas are important natural environments for a vast variety of wildlife, as they provide shelter, act as nurseries for many species of animals, and are an important source of food for both animals and humans [152]. Areas near large coastal cities and near rivers which carry pollution from numerous WWTPs located inland are likely to be affected by micropollutants. However, coastal areas with low populations, as is the case for small countries like New Zealand, may also be affected by sewage pollution. There is a lack of information on the presence of

micropollutants in the New Zealand aquatic environment. In addition, to our knowledge no research has previously been conducted on the presence of the target micropollutants in the Antarctic environment.

The overall aims of this thesis were to determine the concentrations of target micropollutants in Whakaraupo Harbour, New Zealand, and Erebus Bay, Antarctia. By studying two vastly different environments using the same methodology it will allow reliable comparisons to be made and to identify factors may be important in controlling the concentrations, fate and behaviour of micropollutants.

Specific objectives were as follows:

1. To determine the concentrations of micropollutants in the effluent of three WWTPs discharging into Whakaraupo Harbour, and their distribution in the receiving seawater, sediments, and biota.

2. To determine the concentration of micropollutants in the WWTP effluents of Scott Base and McMurdo Station, and their distribution in the seawater and biota of the receiving environment.

3. To compare and contrast the data from these two different environments.

4. To determine how varying light and temperature levels may affect the photodegradation of micropollutants, and apply these findings to low light and low temperature conditions found in Antarctica.

1.6.1 Thesis Structure

This thesis is presented in five chapters following this introduction.

Chapter 2 describes the analytical methods for the selected analytes in water, sediment, and biota samples. The work carried out to re-validate each method for this particular work is also presented in this chapter.

Chapter 3 presents the results of an investigation of micropollutants in Whakaraupo Harbour seawater, sediments, biota, and sewage effluent released into the harbour via three WWTPs. Seasonal and temporal trends observed in these matrices, in particular the WWTPs effluents, are discussed and compared to international studies.

Chapter 4 presents the Antarctic component of this thesis, and presents the results of two field studies conduced during the 2009/2010 and 2012/2013 Antarctic research season in Erebus Bay. The presence of micropollutants was investigated in WWTP effluents of two Antarctic

research stations, the seawaters of Erebus Bay, and marine biota. These results are critically compared to the results in Chapters 3.

Chapter 5 describes the work conducted to understand the potential role photodegradation can play in the degradation of micropollutants, and how low levels of light and temperature may affect this process.

The overall conclusions with reference to the objectives of the research, and recommendations for future research, are presented in Chapter 6.

CHAPTER TWO

METHODOLOGIES

2 Methodologies

2.1 Introduction

This chapter describes in detail all the experimental methods used for this thesis. The solid phase extraction protocol was used for all seawater and sewage effluent samples from Whakaraupo Harbour and Antarctica, and was also used as a clean-up step for the sediment and biota samples. The accelerated solvent extraction method was used to extract the sediments and biota collected during the course of this thesis, and was carried out at Plant & Food Research Ruakura, Hamilton. All samples were analysed at the University of Canterbury using the GC-MS method developed in-house. This chapter also describes the experimental procedures for the photodegradation experiments which were carried out at CSIRO Adelaide in 2011 and 2013.

Details of the fieldwork including sampling protocols and sampling locations for the Whakaraupo Harbour study and the two Antarctic field seasons are not described in this chapter as these vary for each of the three studies. Instead, this information is provided in the respective thesis chapters.

The solid phase extraction method and accelerated solvent extraction method were developed by the US Environmental Protection Agency, adapted at Plant & Food Research Ruakura, Hamilton, and re-validated at the University of Canterbury. The GC-MS analysis method and the sample derivatisation protocols were developed by Dr. Lisa Graham at the University of Canterbury with assistance provided by the work from this thesis [153].

2.2 Solid Phase Extraction

2.2.1 Chemicals

Solid standards of *p*-hydroxybenzoic acid methyl ester (mParaben, purity 97.5%), *p*-hydroxybenzoic acid ethyl ester (eParaben, purity 100%), *p*-hydroxybenzoic acid propyl ester (pParaben, purity 99.8%), and *p*-hydroxybenzoic acid butyl ester (bParaben, purity 100%), 4-methyl-benzylidene camphor (4-MBC, purity 100%), 2-hydroxy-4-methoxybenzophenone (BP-3, purity 100%), and octyl-methoxycinnamate (OMC, purity 100%) were purchased from AccuStandard (New Haven, CT). Solid standards of 2,4-dihydroxybenzophenone (BP-1, purity 99%), 3-phenoxybenzyl alcohol (3-PBOH, purity 98%), 2,2-bis(4-hydroxyphenyl)propane (BPA, purity >99%), 4-*n*-nonylphenol (NP, purity 99.9%), estrone (E1, purity >99%), 17β-estradiol (E2, purity >98%), estriol (E3, purity 99%), 17α-ethinylestradiol (EE2, purity <98%), and the internal standard 2,2-bis(4-hydroxy-3-methylphenyl)propane (BPC, purity 97%) were purchased from Sigma Aldrich (St. Louis,

MO). Three further internal standards used for the biota samples were $^{13}C_2$-mono-2-ethylhexyl phthalate ($^{13}C_2$-mEHP, purity 99%), $^{13}C_2$-monoethyl phthalate ($^{13}C_2$-mEP, purity 99%), and $^{13}C_6$-3-phenoxybenzoic acid ($^{13}C_6$-3PBA, purity 99%) and were purchased from Cambridge Isotope Laboratories Inc (Cambridge, UK). Solid standards of 5-chloro-2-(2,4dichlorophenoxy)phenol (triclosan, purity 99.5%), and 2,4,4'-trichloro-2'-methoxydiphenyl ether (mTriclosan, purity 99%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Solid standard of 4-*t*-octylphenol (OP, purity 99.4%) was purchased from Supelco Analytical (Bellefonte, PA). Individual stock standards of each chemical were prepared in ACN. These stock standard solutions were combined and diluted to produce a 1 μg mL^{-1} master mix in ACN for the preparation of calibration curves.

Carbon-13 labelled surrogates of $^{13}C_6$-mParaben (purity >98%), $^{13}C_6$-bParaben (purity >98%), $^{13}C_6$-NP (purity >96%), $^{13}C_{12}$-triclosan (purity >98%), $^{13}C_{12}$-BPA (purity >98%), and $^{13}C_6$-E2 (purity >98%) were purchased from Cambridge Isotope Laboratories Inc (Cambridge, UK). The surrogates were combined into a 1 μg mL^{-1} master mix in ACN to be added to each sample. The 1 μg mL^{-1} surrogate solution used in the first Antarctic trip did not contain $^{13}C_{12}$-triclosan or $^{13}C_6$-E2 as these were not available at the time, and was prepared in acetone.

The solvents used for the different case studies came from a number of different sources. For the Antarctic fieldwork methanol (MeOH), dichloromethane (DCM), and acetone (all UltimAR grade) were purchased from Mallinckrodt Baker Inc (Phillipsburg, NJ). Ultrapure (18MΩ cm^{-1}) MilliQ water (MQ) was sourced from an in-house water purification system (Millipore, USA). Sodium sulfate (puriss. p.a. ACS, anhydrous, granulated) was purchased from Sigma Aldrich.

For the Whakaraupo Harbour case study, HPLC grade MeOH, acetone (Optima) and DCM (Optima) was purchased from Fisher Scientific (Fair Lawn, New Jersey). HPLC/Spectro grade (LeDA) DCM was also purchased from Scharlau Chemie (Sentmenat, Spain), while acetone (pro analysis, ACS grade) was also purchased from Merck (Darmstadt, Germany). Acetonitrile (ACN) was purchased from Merck (LiChrosolv, LC Grade) and from Romil Pure Chemistry (SpS Super Purity). Ultrapure water (Sartorius Stedim, Arium® pro UV, Biotech) was primarily used. However ultrapure (18MΩ cm^{-1}) MilliQ water (MQ) was sourced from a second in-house water purification system (Millipore, USA) while the other in-house source had to be serviced. Sodium sulfate (anhydrous, granulated, 10 – 60 Mesh) was purchased from Mallinckrodt.

Sulphuric acid (conc ACS reagent) was purchased from Mallinckrodt Baker Inc (Phillipsburg, NJ). Decon90 (5 L) was purchased from Decon Laboratories Ltd (Sussex, UK). These chemicals were used in all case studies.

2.2.2 Materials

Solid phase extraction cartridges (Oasis HLB, 1g/20mL) were purchased from Waters. Florisil (synthetic magnesium silicate) clean-up cartridges (1g/6mL, mesh <250 μm) were purchased from IST Isolute. GF/C filter papers were purchased from Whatman.

2.2.3 Sample Extraction

The seawater and sewage effluent samples were extracted within at most 48 hours as recommended by the U.S. Environmental Protection Agency [154]. The samples were acidified to pH 2 within 12 hours of sampling with concentrated sulphuric acid, and vacuum filtered through a GF/C filter (Whatman). Prior to extraction the 1 L (effluent), 4 L (seawater), and 10 L (seawater) samples were spiked with 50 μL, 100 μL, or 250 μL respectively of the 1 μg mL^{-1} surrogates solution ($^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2). Solid phase extraction (SPE) cartridges (Waters, Oasis HLB, 1g/20mL) were pre-rinsed with 4 x 10 mL DCM/MeOH (95:5), dried under vacuum, and conditioned by the addition and elution of 2 x 10 mL MeOH followed by 2 x 10 mL MQ water. Samples were extracted on a VacMaster Sample Processing Station (Biotage) by connecting the sample container and SPE cartridge with a transfer tube and passing the sample through the cartridge at a flow rate of 15 – 20 mL min^{-1} under vacuum (Figure 2.1). After extraction the cartridges were dried under full vacuum (~3 – 4 hours). Sodium sulfate cartridges (prepared in house) and florisil cartridges (IST Isolute Florisil, 1g/6mL) were washed with 2 x 5 mL acetone, then dried under vacuum. The HLB cartridges were connected to the top (in order of HLB – sodium sulfate – florisil) and eluted with 6 x 5 mL DCM/MeOH (95:5) into silanised 30 mL amber glass vials (Figure 2.2). The sample vials were capped and stored at -80°C until GC-MS analysis. At Scott Base the samples were stored at -20°C in the Scott Base Science Freezer until transport back to New Zealand where they were also stored at -80°C.

Figure 2.1: SPE extraction set up of 4 L seawater samples.

Figure 2.2: SPE elution set-up. From top to bottom: HLB cartridges, sodium sulfate, florisil.

2.2.4 QA/QC

All glassware was solvent rinsed prior to use. During the first Antarctic field trip all glassware was rinsed three times with first MeOH, DCM, hexane, and lastly acetone. The cleaning regime was changed to three times MeOH and ACN for the remainder of the work presented in this thesis. The sodium sulfate and GF/C filter papers were rinsed with MeOH and ACN prior to use. In addition the sodium sulphate was baked overnight at 500°C. This step was observed to significantly reduce any blank contributions of analytes, in particular BP-3, BP-1 and BPA.

A number of quality control samples were prepared alongside the environmental samples. For the seawater samples two locations were always sampled and extracted in duplicate for each sampling round. Sewage effluents from each WWTP (New Zealand and Antarctica) were

always sampled in duplicate. At least one further sample of seawater or sewage effluent was also spiked with a known amount of analyte (100 μL or 250 μL of 1 μg mL^{-1} mix for seawater and sewage effluent samples respectively). One sample of seawater was also spiked with a low amount of analyte (10 μL) to aid in GC/MS peak qualification. Every extraction batch included a trip blank, a MQ and cartridge blank and spike (1 L during sewage sampling, 4 L during seawater sampling). All environmental samples, including the trip blank, MQ and cartridge blanks, were spiked with the same volume of 1 μg mL^{-1} ^{13}C-labeled surrogate solution as the samples to check the analyte recovery of the SPE method. The trip blank, MQ and cartridge blanks, as well as the MQ and cartridge spikes (spiked with the same amount analyte as the sample spikes) were extracted at the same time as the samples. Comparative standards were dispensed at the same time as the corresponding set of samples were spiked prior to extraction. During elution of the cartridges a sodium sulfate cartridge blank, and a solvent blank, were also prepared. All reported results were corrected for analyte contributions quantified in the cartridge blank. Quality control measures during the first Antarctic field trip only involved duplicate sample extractions, MQ blanks, and comparative standards.

2.2.5 Method Validation

The method was validated for three sample volumes, 1 L (sewage effluent volume), 4 L (New Zealand and Antarctic seawater volume), and 10 L (Antarctic seawater volume). The spike volume was adjusted according to the volume of water to be extracted. Seven replicate 1 L MQ, and 4 L and 10 L seawater samples were spiked with 50 μL, 100 μL, and 250 μL respectively of 1 μg mL^{-1} analyte and surrogate solution. A further seven blank replicates were spiked with the same amount of surrogate solution and extracted alongside the spiked samples. Any blank contribution was averaged and subtracted from the spikes before the spike recoveries were reported. Due to the large volume of seawater which needed to be processed the 4 L and 10 L validations were divided into two and three batches respectively. The spike and blank samples were divided equally between each batch. The recoveries of all analytes and surrogates were within an acceptable range for all volumes (Defined as ~70% - 120% [155], Table 2.2a and Table 2.2b). However the recoveries of most compounds were lower at 10 L than at 4 L. This is most likely due to overloading of the cartridges given the large volume of sample. Almost all %RSDs were below 15%, though most were below 10%. Analytes which showed the most variability were BP-3 and BPA. This was most likely due to their widespread occurrence in the environment and from background laboratory contributions. The recovery of E1 was slightly outside the acceptable maximum recovery of 120% for the 4 L samples. The likely reason for this is explained in detail in Section 2.4.6.

However high recoveries of steroid hormones have been reported previously by other research groups [156].

Table 2.1: Limits of quantification of analytes in seawater and WWTP effluent, with lower and upper limits at 95% confidence.

Analyte	Limit of Quantification (Seawater, ng L^{-1})	Lower limit	Upper limit	Sewage recovery surrogate used	Limit of Quantification (Sewage effluent, ng L^{-1})	Lower limit	Upper limit
mParaben	0.82	0.53	1.82	$^{13}C_6$-mParaben	0.67	0.43	1.48
eParaben	0.43	0.28	0.95	$^{13}C_6$-mParaben	0.67	0.43	1.48
OP	0.21	0.14	0.47	$^{13}C_{12}$-Tric	1.52	0.97	3.35
pParaben	0.82	0.53	1.81	$^{13}C_6$-bParaben	1.29	0.83	2.84
bParaben	0.45	0.29	0.98	$^{13}C_6$-bParaben	1.29	0.83	2.84
NP	0.44	0.29	0.98	$^{13}C_6$-NP	1.65	1.05	3.62
4-MBC	3.18	2.04	7.00	$^{13}C_{12}$-Tric	1.52	0.97	3.35
BP-3	2.64	1.69	5.82	$^{13}C_{12}$-BPA	0.28	0.18	0.62
mTric	0.22	0.14	0.48	$^{13}C_{12}$-Tric	1.52	0.97	3.35
Tric	0.54	0.35	1.2	$^{13}C_{12}$-Tric	1.52	0.97	3.35
BP-1	0.78	0.50	1.72	$^{13}C_{12}$-BPA	0.28	0.18	0.62
BPA	1.27	0.81	2.79	$^{13}C_{12}$-BPA	0.28	0.18	0.62
OMC	1.92	1.23	4.23	$^{13}C_{12}$-Tric	1.52	0.97	3.35
E1	7.00	4.48	15.4	$^{13}C_6$-E2	0.68	0.43	1.49
E2	0.43	0.28	0.95	$^{13}C_6$-E2	0.68	0.43	1.49
EE2	1.42	0.91	3.12	$^{13}C_6$-E2	0.68	0.43	1.49
E3	2.05	1.31	4.52	$^{13}C_6$-E2	0.68	0.43	1.49

Table 2.2a: Spike recoveries and statistical summary of analytes from 1 L MQ, and 4 L and 10 L seawater.

Analyte	Average % Recovery (MQ water, 1 L, n=7)	Std dev	%RSD	95% C.I.	Average % Recovery (Seawater, 4 L, n=6)	Std dev	%RSD	95% C.I.	Average % Recovery (Seawater, 10 L, n=7)	Std dev	%RSD	95% C.I.
mParaben	73.9%	9.5%	12.9%	8.8%	81.9%	6.8%	8.3%	7.1%	58.1%	8.0%	13.7%	7.4%
eParaben	80.0%	7.9%	9.9%	7.3%	89.0%	5.2%	5.9%	5.5%	76.0%	1.6%	2.1%	1.5%
OP	67.6%	9.3%	13.7%	8.6%	91.3%	9.2%	10.1%	9.7%	74.9%	5.5%	7.3%	5.1%
pParaben	85.5%	5.2%	6.1%	4.8%	97.5%	3.8%	3.9%	4.0%	85.2%	6.0%	7.0%	5.5%
bParaben	82.9%	2.5%	3.1%	2.3%	85.0%	4.7%	5.6%	5.0%	65.2%	7.2%	11.1%	6.7%
NP	66.9%	4.0%	5.9%	3.7%	60.7%	7.3%	12.0%	7.7%	75.7%	9.0%	12.0%	8.4%
4-MBC	89.2%	3.5%	4.0%	3.3%	118.7%	12.0%	10.11%	12.60%	75.1%	5.4%	7.1%	5.0%
BP-3	82.3%	2.2%	2.7%	2.1%	124.4%	13.4%	10.8%	14.0%	55.8%	12.9%	23.1%	11.9%
mTric	80.3%	2.7%	3.3%	2.5%	99.7%	2.8%	2.8%	2.9%	53.7%	4.0%	7.4%	3.7%
Tric	80.4%	1.5%	1.9%	1.4%	106.8%	8.7%	8.2%	9.1%	104.5%	2.8%	2.7%	2.6%
BP-1	92.3%	13.1%	14.2%	12.2%	123.5%	11.6%	9.4%	12.1%	93.6%	3.7%	3.9%	3.4%
BPA	93.2%	8.8%	9.4%	8.1%	79.2%	11.3%	14.1%	11.8%	53.4%	20.6%	38.5%	19.0%
OMC	69.2%	6.1%	8.8%	5.6%	94.5%	4.8%	5.1%	5.1%	52.3%	9.8%	18.7%	9.0%
E1	79.3%	15.0%	19.0%	13.9%	142.9%	7.8%	5.5%	8.2%	120.9%	5.1%	4.2%	4.7%
E2	91.6%	4.3%	4.7%	4.0%	94.9%	1.2%	1.2%	1.2%	74.1%	7.6%	10.3%	7.0%
EE2	102.3%	2.6%	2.5%	2.4%	115.5%	0.9%	0.8%	0.9%	121.3%	4.9%	4.1%	4.6%
E3	107.7%	2.6%	2.4%	2.4%	102.0%	3.1%	3.0%	3.2%	95.5%	3.9%	4.1%	3.6%

Table 2.2b: Spike recoveries and statistical summary of surrogates from 1 L MQ, and 4 L and 10 L seawater.

Isotope Surrogates	Average % Recovery (MQ water, 1 L, n=7)	Std dev	%RSD	95% C.I.	Average % Recovery (Seawater, 4 L, n=13, *n=12)	Std dev	%RSD	95% C.I.	Average % Recovery (Seawater, 10 L, n=11)	Std dev	%RSD	95% C.I.
mParaben (ring $^{13}C_6$)	81.1%	9.4%	11.6%	8.7%	81.0%*	6.8%	8.4%	4.3%	90.7%	5.9%	6.5%	4.0%
bParaben (ring $^{13}C_6$)	90.5%	2.5%	2.8%	2.3%	84.8%	5.6%	6.6%	3.4%	93.2%	3.4%	3.7%	2.3%
NP (ring $^{13}C_6$)	68.2%	5.0%	7.4%	4.6%	56.1%	4.5%	8.0%	2.7%	65.3%	5.3%	8.0%	3.5%
Tric (ring $^{13}C_{12}$)	87.5%	2.4%	2.8%	2.2%	104.4%	5.5%	5.3%	3.3%	98.6%	3.6%	3.6%	2.4%
BPA (ring $^{13}C_{12}$)	105.9%	5.6%	5.3%	5.1%	93.3%	6.6%	7.1%	4.0%	76.1%	3.8%	4.9%	2.5%
E2 (ring $^{13}C_6$)	89.2%	3.1%	3.5%	2.9%	89.7%	1.5%	1.7%	0.9%	69.7%	23.4%	33.6%	15.7%

2.2.6 Limits of Quantification

Limits of quantification were determined using EPA guidelines [157] and are presented in Table 2.1. Seawater samples were sourced off the coast of Banks Peninsula (~7 km) to obtain samples containing the lowest level of analyte possible. Seven replicates were spiked at five times the estimated instrumental detection limit and processed as samples. In addition seven unspiked seawater samples were processed to account for matrix contributions. The limit of quantification was defined as the standard deviation of the seven replicates multiplied by the student t-value for n = 7 at $\alpha = 0.01$ (3.143). The upper and lower 95% confidence limits of this distribution were calculated using the chi-squared distribution for n = 7. Due to the high background levels of analytes in sewage effluents, carbon-labelled spikes were used as surrogates to determine the sewage effluent limits of quantification. Surrogates were matched to target analytes according to structural similarities, and are provided in Table 2.1.

Quantification limits are provided in Table 2.1, and in seawater ranged between 0.21 ng L^{-1} for OP to 7 ng L^{-1} for E1, and in sewage effluent between 0.28 ng L^{-1} ($^{13}C_{12}$-BPA surrogate) to 1.52 ng L^{-1} ($^{13}C_{12}$-Tric surrogate). E1 was found to be highly sensitive to the condition of the injection liner, resulting in a high quantification limit for E1. This is discussed further in Section 2.4.6.

2.3 Accelerated Solvent Extraction Methodology

2.3.1 Chemicals

HPLC grade MeOH (Optima), DCM (submicron filtered), acetone (submicron filtered), isopropanol (IPA)(submicron filtered) and pentane (pesticide grade) were purchased from Fisher Scientific. Isopropyl alcohol (IPA) (ChromAR grade) was also purchased from Mallinckrodt. MQ water was sourced from the in-house water purification system (Integral 5 Millipore Instrument, USA). Dipotassium phosphate (powder, A.C.S reagent) was purchased from J.T. Baker. Potassium dihydrogen phosphate (monobasic, molecular biology grade) was purchased from Sigma. Sodium sulphate (anhydrous, granular 10 – 60 mesh, AR grade) was purchased from Mallinckrodt. Celite was purchased from Sigma. Diatomaceous earth and Ottawa sand were purchased from Restek. SX8 biobeads for GPC were purchased from BioRad.

2.3.2 Materials

Solid phase extraction cartridges (Oasis HLB, 1g/20mL) were purchased from Waters. Florisil clean-up cartridges (2g/15mL) were purchased from IST Isolute. GF/C filter papers

and high purity glass microfiber Accelerated Solvent Extraction (ASE) thimbles (19mm internal diameter x 90mm external length) were purchased from Whatman. ASE cellulose filter papers were purchased from Dionex.

2.3.3 Sample Preparation and Extraction

The sediment and biota samples were thawed overnight at 4°C prior to extraction. The thawed sediments were packed into pre-weighed ASE cells fitted with an extraction filter and thimble. The cell was weighed again and the weight of packaged sediment recorded (~20 g). The sample was then topped with a layer of pre-cleaned Ottawa sand (~1 – 2 mm). Biota samples were homogenized before extraction. Biota samples (~ 8 g) were prepared in the same way, however the bottom of the thimble was lined with a layer of celite and diatomaceous earth. In addition the biota samples were topped with a second layer of diatomaceous earth followed by a layer of Ottawa sand and a second extraction filter (~1 – 2 mm for each layer). Before extraction all samples were spiked with 100 μL of the 1 μg mL^{-1} surrogates solution ($^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2), which was added to the top of the Ottawa sand layer. The cells were then sealed and loaded on to the ASE instrument.

The samples were extracted on an ASE 200 Accelerated Solvent Extractor (Dionex, Sunnyvale, CA, USA) fitted with a Dionex Solvent Controller, and operated using the Dionex AutoASE software (Release 2.2). Each cell was extracted once using two extraction procedures. All samples were subjected to the first extraction procedure before commencing the second. The first extraction conditions were: 10 minutes static mode (2 cycles) with H_2O/IPA (50:50) at 120°C and 1450 PSI, 60% flush volume and 30 seconds purge time. The second extraction conditions were: 10 minutes static mode (2 cycles) with H_2O/IPA (20:80) at 180°C and 1450 PSI, 60% flush volume and 30 seconds purge time. The extracts from each extraction procedure were collected into separate vials. Prior to extraction the vials for the second extraction were filled with 3 mL of pentane to help prevent the hot H_2O/IPA extract from evaporating as the pentane forms the top layer of the mixture.

2.3.4 Solid Phase Extraction Clean-Up

The two ASE extracts of the sediments were combined into a 500 mL Schott bottle. Each vial was rinsed twice with 50 mL phosphate buffer (pH = 7) and the rinsate added to the extract. The combined biota extracts and the rinse buffer were filtered (e.g. precipitated protein) through a pre-cleaned (DCM and acetone) GF/C filter paper, topped with solvent cleaned celite to prevent clogging of the filter paper. Solid phase extraction (SPE) cartridges (Waters, Oasis HLB, 1g/20mL) were pre-rinsed with 2 x 10 mL DCM/MeOH (95:5), dried under

vacuum, and conditioned by the addition and elution of 2 x 10 mL MeOH followed by 2 x 20 mL MQ water. Samples were extracted on a VacMaster Sample Processing Station (Biotage) by connecting the sample container and SPE cartridge with a transfer tube and passing the sample through the cartridge at a flow rate of 15 – 20 mL min^{-1} under vacuum. After extraction the cartridges were dried under full vacuum (~3 – 4 hours). Florisil cartridges (IST Isolute Florisil, 2g/15mL) were topped up with pre-baked sodium sulfate and washed with 2 x 10 mL acetone, then dried under vacuum. The HLB cartridges were connected to the top of the florisil cartridge and eluted with 3 x 5 mL DCM/MeOH (95:5), followed by 1 x 15 mL DCM/MeOH (95:5) into 30 mL amber glass vials. The sample vials were capped and stored at 4°C until gel permeation chromatography (GPC) clean-up.

2.3.5 Gel Permeation Chromatography Clean-Up

The 30 mL extracts were reduced to near-dryness under N_2 and gentle heating (40°C) before being quantitatively transferred with 5 x 0.25 mL DCM/MeOH (95:5) into champagne glass shaped GPC vials. The vials were made up to the top of the vial neck (~1500 µL) with DCM/MeOH (95:5) and stored at 4°C until injection. All ASE samples were subjected to gel permeation chromatography (GPC) using a Shimadzu Class VP GPC system controlled by a SCL-10A VP System Controller and fitted with a LC-10AT VP Liquid Chromatograph interfaced to a SIL-10AP Auto Injector, a SPD-10A UV-Vis Detector, and a FRC-10A Fraction Collector. Instrumental control and UV-Vis data processing were performed by the Shimazdu Class VP software (Version 6.14 SP2). Injected samples (set at 1550 µL) were separated from the co-extracted matrix on two GPC columns containing SX8 Biobeads (prepared in-house, 1 x 44 cm each) connected in series. DCM/MeOH (95:5) was used as the mobile phase at a flow rate of 1.5 mL min^{-1}. The sample elution was monitored at 254 nm and the sample fraction between 21 – 32 minutes was collected. The collection window was checked prior to GPC clean-up with the injection of 250 µL of a 0.5 µL mL^{-1} standard mixture. The collected fraction was reduced to near-dryness under N_2 and gentle heating before a quantitative transfer with 4 x 0.25 mL DCM/MeOH (95:5) into amber HPLC vials and stored at -20°C until GC-MS analysis.

2.3.6 Dry Weight Determination

Dry weights of the biota and marine sediments were determined according to the National Ocean and Atmospheric Administration (NOAA) guidelines [158]. Approximately 2 – 5 g of wet homogenized biota tissue (0.2 – 0.3 g for the limited Antarctic biota) or 3 – 6 g of wet marine sediment was weighed into dry labelled pre-weighed aluminium dishes. The dry weights of all samples were determined in duplicate. The samples were dried in a 105°C oven for 24 hours followed by cooling in a desiccator for at least 10 minutes prior to weighing.

Samples were placed back in the oven for a further 24 hours at 105°C, cooled in a desiccator and weighed again. This was repeated until successive weight differences were less than 4% (48 hours).

2.3.7 Lipid Determination

The lipid contents of the biota samples were determined using methodology created in-house. After the ASE for the determination of target analytes was completed, the sample cell was extracted using DCM. The ASE conditions were: 5 minutes static mode (2 cycles) with DCM at 100°C and 2000 PSI, 60% flush volume and 20 seconds purge time. The extracts were collected into pre-weighed sample vials and evaporated to dryness under N_2 gas on a TurboVac (Caliper Life Sciences). The vials were then dried further in a 50°C oven for 24 hours before the vials were weighed and the amount of extracted lipids recorded.

2.3.8 QA/QC

Each ASE batch comprised of twelve samples. One marine sediment or biota duplicate and a spike sample (100 μL of the 1 μg mL^{-1} standard solution) was included in every two ASE batches. ASE extraction cell blanks filled with Ottawa sand were extracted along with the marine sediment and biota samples. Both cells were spiked with 100 μL of the 1 μg mL^{-1} surrogates solution. One cell was also spiked with 100 μL of the 1 μg mL^{-1} standard solution. A comparative standard was prepared at the same time as the samples were spiked. The celite, diatomaceous earth, Ottawa sand, and cellulose filter papers were solvent extracted on the ASE prior to use. The cellulose thimbles and sodium sulfate was baked overnight at 500°C prior to use. During the SPE clean-up a H_2O/IPA blank was prepared with 200 mL of phosphate buffer and extracted along with the marine sediment and biota ASE extracts. A solvent blank was prepared during elution of the SPE cartridges. The Ottawa sand blanks and spikes, the H_2O/IPA blanks, and solvent blanks were also subjected to GPC clean-up.

2.3.9 Method Validation

As was the case for the SPE method the ASE method was also re-validated for the extraction efficiency of sediment and biota matrices. Reference sediments were obtained from an intertidal lagoon at the western end of Peachgrove Bay, Great Mercury Island (North Island). The sediment was sampled by scraping the open side of a glass jar across the top 3cm of the lagoon sediment. Water was decanted and the process repeated until suitable quantity of sediment was obtained. The sediment was stored in a refrigerator for one day before being transported to Plant and Food Ruakura, Hamilton, and frozen. The reference green lipped mussels were taken during a receding tide from a rocky shoreline shelf at the far eastern end of Otama Beach, Corromandel Peninsula (North Island) while wearing neoprene diving

gloves. The mussels were placed in polyethylene plastic bags and frozen within 20 minutes of collection. The mussel tissues were homogenized using an UltraTurex prior to use. A spike volume of 100 μL of 1 μg mL^{-1} analyte and surrogate solution was set. Seven replicates were spiked with surrogate solution and extracted alongside an additional seven replicates spiked with both anlayte and surrogate solution. Any blank contributions were averaged and subtracted from the spikes before the spike recoveries were reported. Spike recoveries were calculated against the comparative standard prepared at the time of sample spiking.

Recovery efficiencies for sediments were at acceptable levels except for the UV filter OMC, which on average was only 32.2% (Table 2.3a). Overall the extraction variability was higher than those for the water samples, with most %RSDs between 10 – 20 %. However these are acceptable give the more complex sample matrix and the extra clean-up steps, which these samples have undergone, compared to water extracts. Similarly, all surrogates were sufficiently recovered with %RSDs also mostly ranging between 10 – 20% (Table 2.3b).

The recoveries of the biota replicates were heavily influenced by the complicated biota matrix. Analytes and surrogates eluting in the first third of the GC-MS chromatograph were recovered at levels and variabilities comparable to those for sediments (Table 2.3a). Most analytes and surrogates eluting in the second third were not recovered (NP, 4-MBC, BPA, and OMC) or were recovered at reduced levels (BP-3, mTric, Tric, BP-1, $^{13}C_6$-NP, and $^{13}C_{12}$-BPA). A review of extraction methodologies for UV-filters in biota has observed extraction efficiencies were influenced by lipid content, with higher recoveries achieved when lipid contents were lower [109]. The steroid hormones, eluting in the last third of the chromatograph, were also recovered at reduced levels, except EE2. The last two thirds of the chromatographic region showed signs of large matrix interferences, most likely lipids and proteins that were not completely removed during the clean-up steps. These compounds were present at such high concentrations their fragmentation ions swamped out those originating from the analytes. Due to these factors this analytical method was only able to qualitatively report on approximately two thirds of the original number of analytes in biota, and quantitatively report on mParaben, eParaben, OP, pParaben, bParaben, BP-3, BP-1, E2, and EE2.

Table 2.3a: Spike recoveries and statistical summary of analytes using a reference lagoon sediment and reference green lipped mussel composite.

	Lagoon sediments				Mussels			
Analyte	Average % Recovery (n=7)	Std dev	%RSD	95% C.I.	Average % Recovery (n=7)	Std dev	%RSD	95% C.I.
mParaben	105.8%	14.2%	13.4%	13.2%	95.8%	11.9%	12.4%	11.9%
eParaben	93.8%	11.8%	12.5%	10.9%	90.8%	7.7%	8.5%	7.7%

OP	120.3%	20.1%	16.7%	18.5%	83.1%	20.2%	24.3%	20.2%
pParaben	98.6%	12.4%	12.5%	11.4%	85.5%	7.3%	8.6%	7.3%
bParaben	63.5%	19.3%	30.4%	17.8%	89.2%	4.7%	5.3%	4.7%
NP	74.6%	13.0%	17.5%	12.0%	NR	–	–	–
4-MBC	95.3%	14.8%	15.5%	13.7%	NR	–	–	–
BP-3	88.1%	7.9%	9.0%	7.3%	53.1%	6.4%	12.0%	6.4%
mTric	73.0%	10.6%	14.5%	9.8%	30.3%	4.7%	15.4%	4.7%
Tric	57.4%	11.6%	20.2%	10.7%	44.9%	10.3%	23.0%	10.3%
BP-1	62.1%	8.2%	13.2%	7.6%	67.2%	15.3%	22.8%	15.3%
BPA	78.2%	17.7%	22.6%	16.3%	NR	–	–	–
OMC	68.0%	9.3%	13.7%	8.6%	NR	–	–	–
E1	60.5%	5.7%	9.4%	5.3%	47.7%	20.8%	43.7%	12.5%
E2	71.4%	5.3%	7.4%	4.9%	56.9%	26.2%	46.0%	26.1%
EE2	80.0%	3.0%	3.8%	2.8%	70.0%	27.7%	39.5%	27.6%
E3	100.5%	27.2%	27.1%	25.2%	37.6%	15.7%	41.8%	15.7%

Table 2.3b: Spike recoveries and statistical summary of surrogates using a reference lagoon sediment and reference green lipped mussel composite.

	Lagoon sediments				Mussels			
Isotope Surrogates	Average % Recovery (n=14)	Std dev	%RSD	95% C.I.	Average % Recovery (n=14)	Std dev	%RSD	95% C.I.
mParaben (ring $^{13}C_6$)	113.7%	21.8%	19.2%	12.6%	91.7%	13.9%	15.1%	8.3%
bParaben (ring $^{13}C_6$)	103.5%	16.5%	15.9%	9.5%	78.3%	4.7%	6.0%	2.8%
NP (ring $^{13}C_6$)	82.1%	10.5%	12.7%	6.0%	NR	–	–	–
Triclosan (ring $^{13}C_{12}$)	87.3%	12.0%	13.7%	6.9%	46.7%	8.4%	18.0%	5.1%
BPA (ring $^{13}C_{12}$)	61.0%	26.2%	42.9%	15.1%	NR	–	–	–
E2 (ring $^{13}C_6$)	64.8%	7.7%	11.9%	4.5%	44.3%	24.1%	54.5%	24.1%

2.3.10 Limits of Quantification

The SPE quantification limits identified in Section 2.2.6 (Table 2.1) were used to calculate the limits of quantification in the sediment and biota samples. In Table 2.1 the limits of quantification are expressed in ng L^{-1} (e.g. 0.82 ng L^{-1} for mParaben), while the GC-MS calibration curve quantifies the injected sample in absolute ng (Section 2.4.5). During the GC-MS data analysis the quantifiable amount mParaben in a 4 L seawater sample is therefore 3.2 ng (0.82 ng L^{-1} x 4 L). Similarly, any sediment or biota sample analysed on the GC-MS with a mParaben concentration above 3.2 ng was considered quantifiable. Quantification limits for the sediments (Table 2.4) were calculated using this approach for all analytes using a fixed sample weight of 20 g wet weight (14 g dry weight assuming 70% dry weight). Similarly, the biota quantification limits (Table 2.4) were calculated with a fixed sample weight of 8 g wet weight (1.6 g dry weight assuming 20% dry weight).

Table 2.4: Limits of quantification (ng g^{-1} wet weight and dry weight) for the described ASE protocol for marine sediment and biota samples, calculated using GC-MS limits of quantification.

Analyte	Sediments		Biota	
	wet weight	dry weight	wet weight	dry weight
mParaben	0.16	0.23	0.41	2.05
eParaben	0.10	0.12	0.22	1.08
OP	0.04	0.06	0.11	0.53
pParaben	0.16	0.23	0.41	2.05
bParaben	0.09	0.13	0.23	1.13
NP	0.09	0.13	0.22	1.10
4-MBC	0.64	0.91	1.59	7.95
BP-3	0.53	0.75	1.32	6.60
mTric	0.04	0.06	0.11	0.55
Tric	0.11	0.15	0.27	1.35
BP-1	0.16	0.22	0.39	1.95
BPA	0.25	0.36	0.64	3.18
OMC	0.38	0.55	0.96	4.80
E1	1.40	2.00	3.50	17.50
E2	0.09	0.12	0.22	1.08
EE2	0.28	0.41	0.71	3.55
E3	0.41	0.59	1.03	5.13

2.4 GC-MS Analysis

2.4.1 Chemicals

N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and N-trimethylsilylimidazole (TMSI) (25 mL) were purchased from Supelco Analytical. Acetonitrile (ACN) was purchased from Merck (LiChrosolv, LC Grade) and from Romil Pure Chemistry (SpS Super Purity). HPLC grade acetone (Optima) and DCM (Optima) was purchased from Fisher Scientific (Fair Lawn, New Jersey). HPLC/Spectro grade (LeDA) DCM was also purchased from Scharlau Chemie (Sentmenat, Spain), while acetone (pro analysis, ACS grade) was also purchased from Merck (Darmstadt, Germany). HPLC grade ethyl acetate was purchased from Scharlau Chemie. Helium gas (Instrument Grade) was purchased from Southern Gas.

2.4.2 Materials

GC glass liners (splitless, single taper gooseneck with wool, 3.5mm x 5.0 x 95) and septa (BTO Shimadzu Plug) were purchased from Restek. The GC injection needle (10 μL) was purchased from SGE Analytical Science. The Techna Sample Concentrator with integrated heating blocks was purchased from Bibby Scientific Ltd (Staffordshire, UK).

2.4.3 Sample Derivatisation

Prior to analysis, samples were reduced to near-dryness under N_2 and gentle heating (~40°C) before a quantitative transfer with 3 x 0.5 mL DCM/MeOH (95:5) into silanised glass derivatisation vials. Samples were then fully dried under N_2, followed by the addition of 100 μL internal standard (BPC, 1 μg mL^{-1}) and 200 μL derivatisation reagent (BSTFA/TMSI, 98:2) and heating (60 minutes at 80°C). Samples were allowed to cool for 10 minutes before being transferred into HPLC vials fitted with glass inserts for analysis. Each derivatisation batch of 24 samples included a 10 and 100 μg L^{-1} analytical standard to act as a derivatisation check, as well as a derivatisation blank (100 μL of ACN).

2.4.4 Instrumental Analysis

The derivatised sample extracts and calibration standards were analysed by gas chromatography/mass spectrometry (GC-MS) using a Shimadzu GC-2010 Gas Chromatograph, interfaced to a Shimadzu AOC-20i Auto Injector and a Shimadzu GCMS-QP2010Plus detector. Instrumental control, data acquisition and data processing were performed using the Shimadzu GCMS Solution software (Version 2.70). Analytes were separated on a Rxi-5Sil column (5% diphenyl/95% dimethyl polysiloxane) 30m x 0.25mm ID, 0.25μm film thickness, with an integrated guard column (10 m, Integra-Guard)(Restek, Belleftone USA). 1 μL volumes of derivatised samples and calibration standards were injected into the injection port in splitless mode at a temperature of 250°C. The splitless time was 1 min, while the split flow rate was 50 – 100 mL min^{-1}. The initial oven temperature of 100°C was held for 5 min, then increased at a rate of 10°C min^{-1} to 300°C where it was held for 20 min, for a total run time of 45 min. Helium was used as the carrier gas at a flow rate of 5.5 mL min^{-1}.

The ion source was held at 200°C and the GC-MS interface at 250°C. Electron Impact Spectra (ESI) was obtained at 70 eV in selected ion mode (SIM). The MS was calibrated against perfluorotributylamine (PFTBA) before each sample run using the mass spectrometry autotune function.

Retention times and m/z ratios used for detection and quantification of the individual compounds are presented in Table 2.5a. Retention times and m/z ratios for the isotopically labelled surrogates are presented in Table 2.5b. Target analytes were quantified against the relative response of the internal standard using an nine-point calibration curve (0, 1, 2.5, 5, 10, 25, 50, 75, and 100 μg L^{-1}) and internal standard quantification.

Table 2.5a: Retention times and SIM mode detection parameters of analytes.

Analyte	Rt (min)	Quantifier ion (*m/z*)	Qualifier ions (*m/z*)
mParaben	12.70	224	209, 177, 193
eParaben	13.66	238	193, 223, 210
mEP $^{13}C_6$ *	14.60	255	227, 181, 166
OP	14.61	207	151, 208, 191
pParaben	14.89	237	210, 193, 252
bParaben	16.11	195	193, 210, 266, 251
3-PBOH	16.98	183	227, 272, 257, 211
NP	17.77	292	180, 165
3PBA $^{13}C_6$ *	18.05	277	233, 292, 203
4-MBC	19.29	254	128, 155, 239
BP-3	19.41	285	286, 242, 223, 180
mEHP $^{13}C_6$ *	19.57	225	227, 153, 243
mTric	19.83	252	302, 254, 232
Tric	19.85	360	345, 362, 310
BP-1	19.98	343	344, 164, 271
BPA	20.57	357	358, 372, 171
BPC*	21.17	385	386, 400
OMC	21.52	178	161, 133, 290
E1	24.23	342	218, 244, 327
E2	24.49	416	285, 129, 326
Coprostane	25.20	217	357, 372
EE2	25.35	425	285, 232, 440
E3	25.97	504	414, 345, 386
Coprostanol	27.00	215	370, 355
Coprostane-3-one	27.80	161	316, 386, 353

* Internal standard

Table 2.5b: Retention times and SIM mode detection parameters of isotopically labelled surrogates.

Isotope surrogates	Rt (min)	Quantifier ion (*m/z*)	Qualifier ions (*m/z*)
mParaben (ring $^{13}C_6$)	12.69	215	230, 199
Butyl paraben (ring $^{13}C_6$)	16.10	216	201, 199, 272
Nonylphenol (ring $^{13}C_6$)	17.76	186	298, 171
Triclosan (ring $^{13}C_{12}$)	19.84	372	359, 374, 322
BPA (ring $^{13}C_{12}$)	20.56	369	370, 384
Estradiol (ring $^{13}C_6$)	24.49	288	422, 332

2.4.5 Calibration Curve

Calibration standards were prepared by adding 100 μL of internal standard of the 1 μg mL^{-1} stock to each derivatisation vial and reduction to dryness under a gentle flow of N_2 and heating (~40°C). Appropriate amounts of calibration standard was then added to create nine calibration standards (100, 75, 50, 25, 10, 5, 2.5, 1, and 0 ng mL^{-1}) and made up to 100 μL with ACN. Standards were derivatised with 200 μL BSTFA/TMSI (98:2) solution using the same procedure as for samples. A fresh set of calibration standards was prepared for each run,

and analysed in the middle of the batch sequence. The full range of calibration standards was injected twice. The chromatogram analyte peaks were referenced against the internal standard to create a nine-point calibration curve with units of absolute ng. The ordinal concentration of each analyte in each standard was entered into the calibration software, with an ordinal concentration of 100 μg L^{-1} used for the internal standard for all samples. The ratio of these concentrations was plotted against the ratio of the target analyte peak area and internal standard peak area. For quantification of an analyte in a real sample the ratio of the analyte peak area and the internal standard of the chromatogram in question was calculated, and the corresponding analyte concentration was automatically reported via the calibration curve by the software. An additional 250 μg L^{-1} standard was added to any sample batch which contained sewage effluent samples for quantification of the sewage effluent spike samples.

The internal standard BPC was used for all sewage effluent, seawater, and marine sediment samples. Three further internal standards were added for the quantification of the biota samples as the complicated matrix gave rise to matrix enhancements in certain parts of the chromatograph which the single internal standard could not correct for. The internal standard mEP-$^{13}C_6$ was used to quantify the analytes mParaben – bParaben. 3PBA-$^{13}C_6$ was used to quantify the analyte NP. mEHP-$^{13}C_6$ was used to quantify the analytes 4-MBC – BP-1. BPC was used for analytes BPA – coprostane-3-one.

2.4.6 Instrumental QA/QC

To maintain optimal instrument analysis conditions a number of quality controls were implemented. Prior to the start of an analysis batch the injection needle was cleaned with acetone and DCM, while the injection port was cleaned with ethyl acetate. Before and after each sample injection the needle was also programmed to rinse three times each with ACN, ethyl acetate, and DCM. E1 was highly sensitive to the condition of the injection liner. Active sites in the GC system, such as free silanol groups and metals, particular in the injection liner, can adsorb some analytes such as thermolabile and polar compounds [58]. Environmental samples tend to contain co-extracted compounds which swamp out these active sites [58]. Clean analytical standards therefore tend to be most affected/suppressed by these active sites, which causes a "matrix enhanced chromatographic response enhancement" in the environmental sample [58]. Similarly these co-extracted compounds can contaminate the glass liner too extensively during extended sample runs, which has been observed to cause signal suppression [159]. These effects were responsible for the high E1 quantification limit presented in Table 2.1. In order to manage this problem analytical standards at 10 and 100 μg L^{-1} were injected at regular intervals (Section 2.4.7), and the E1 peak area was monitored to determine when the liner required replacing. The E1 peak area was recorded after each

sample run. A sudden drop in the recorded E1 peak area (>30%) would indicate the liner required replacing. When the liner was replaced the septum was also replaced. Similarly, non-volatile compounds can accumulate on the front of the GC column and affect peak resolution. The analyte OMC was identified as the indicator for this problem, which manifests as an analyte peak beginning to tail toward the right. Trimming approximately 20 cm off the column before the next instrumental run solved this problem. An analytical standard was run in full ion scan mode after trimming the column to check if the SIM windows need to be adjusted.

2.4.7 Analysis QA/QC

To flush the system of any volatiles which may have accumulated in the system since the previous analysis sequence ended at least two ACN blanks were injected at the beginning of a new sample run. The health of the column was also checked by monitoring the MS with the column held at 200°C in full ion scan mode. A total ion count of approximately 10,000 indicates a healthy column and sample analysis could proceed.

If the liner has been replaced the active sites within the injection port first needed to be stabilised. This was achieved by injection of an analytical standard and an environmental sample, alternating between the two until the E1 peak in the analytical standard has stabilised (~2 – 3 alternating injections). This was then followed by eight further environmental samples, with a repeat injection as the tenth sample. This was followed by a 100 and 10 μg L^{-1} analytical standard, an ACN blank, and eight further environmental samples. The ninth sample was a repeat injection of an environmental sample from the previous set of nine, while the tenth sample was a repeat of the current set. This sequence is repeated (depending on the number of samples available for analysis), followed by a full range of calibration standards (injected twice). After the calibration standards were analysed further environmental samples were analysed until the analytical standard checks indicated E1 was beginning to degrade on the injection liner. In this instance the run was stopped, and the liner and septum replaced. After the injection of several ACN blanks the new active sites are again stabilized as before, and the analysis sequence was continued.

2.4.8 Method Validation

The full details of the GC-MS SIM method development and validation can be viewed in the appropriate sections of the thesis written by Lisa Graham [153].

2.5 Photodegradation Methodology

2.5.1 Chemicals

Solid standards of BPA (>99% purity), EE2 (>98%), triclosan (97%), and 4-*t*-OP (97%) were purchased from Sigma Aldrich (Australia). mParaben (97.7%) was purchased from AccuStandard (New Haven, CT). BP-3 (98%) was purchased from Wako Pure Chemical Industries, Inc. (Japan). Individual stock solutions were prepared at a concentration of 1000 mg L^{-1} in methanol, except for mParaben, which was prepared in ACN. HPLC grade methanol (MeOH) was purchased from Biolab (Australia). Pesticide grade ACN was purchased from Optima. Formic acid (puriss p.a. ~98%) was purchased from Fluka. GF/C filter papers were purchased from Whatman (Australia). Working solutions of the target compounds were prepared in ultrapure (18MΩ cm^{-1}, pH = 6.0) MQ water (Millipore, USA) and in coastal Adelaide seawater (pH ~ 7.5, TOC = 5.3 mg L^{-1}, obtained from the Adelaide pier). The seawater was filtered through a GF/C filter paper, followed by filtration through 0.22 μm syringe filters (ChromTech, 25 mm filter size, nylon membrane).

2.5.2 Preparation of Working Solutions

Target compounds were combined into a single working solution due to the limited space available in the solar simulator, as well as the limited available instrument time. Target compound concentrations were prepared at a nominal 500 μg L^{-1} for mParaben, BPA, BP-3, triclosan, and OP, and at 1000 μg L^{-1} for EE2. Working solutions (3.5 L) were prepared by addition of appropriate amounts of mParaben, BPA, EE2, BP-3, triclosan, and OP of stock solution into 5 L Schott bottles. The solvent was dried off under a gentle stream of N_2 and slight heating until dry. Methanol had to be excluded from the working solutions because of its capacity as a hydrogen source during photodegradation, which has been shown to affect photodegradation at very low concentrations [160, 161]. The bottles were made up to volume with MQ or seawater, and sonicated for 45 minutes to ensure full dissolution of the chemicals. The solutions were left to stand overnight, and subsequently stored at 4°C until and during use. The concentrations of the stock solutions were monitored over time to confirm their stability over the duration of the experiments.

2.5.3 Experimental Design

2.5.3.1 Photochemical Experiments

A series of twelve experiments were carried out. For each experiment, either the temperature or the irradiance level was changed. The experimental key is provided in Table 2.6. Ice had to be used at some environmental conditions to keep the temperature at an appropriate level.

Table 2.6: Key for the temperature and irradiance settings for Experiments 1 to 12.

Experiment #	330 W m^{-2}	500 W m^{-2}	650 W m^{-2}
7°C	1[a]	2[a]	3[a]
14°C	4	5	6[a]
21°C	7	8	9
27°C	10	11	12

[a] ice had to be used to keep the water bath at an appropriate temperature. The ice had to be replenished every half hour.

The experiments were performed in a Suntest Solar Simulator (Atlas Material Testing Technology, USA, Figure 2.3) fitted with a 1500 W xenon lamp. The lamp was fitted with a filter to remove light below 300 nm, a standard procedure for photodegradation experiments to mimic the wavelengths of light which pass through the atmosphere. A water bath was installed into the solar chamber to provide improved control of the experimental temperature. Irradiance levels were monitored with a SLIK SBH-60 SellarNet Inc Radiometer. The temperature of the water bath was monitored with a HOBO Pendant Temperature/Light Data logger (Onset, USA) and remained within ± 2°C of the desired temperature. 50 mL borosilicate glass beakers were used as reaction vessels, and were wrapped in non-reflective material to ensure light entered the beaker through the surface of the test solutions and not through the sides of the beaker. The beaker was also wrapped with aluminium foil to keep the non-reflective wrapping in place. Aliquots of test solution (40 mL) were irradiated in triplicate along with a dark control (beaker with test solution completely wrapped in aluminium foil) and sample blanks (MQ and seawater without target analytes). Subsamples of the irradiated test solutions (1 mL) were collected at 0, 30, 60, 90, 120, 180, 300, and 420 minutes from one MQ water beaker and one seawater beaker. The remaining two triplicate samples, the dark control, and blank beakers were sampled at 0, 60, 180, and 420 minutes to reduce analysis time and costs. Beakers were weighed after each sampling round to correct for volume loss due to evaporation over the experimental period. Samples were stored in labelled amber HPLC vials at 4°C until analysis (within at most six days).

Figure 2.3: Suntest Solar Simulator with view into the solar chamber. The water bath was installed post-purchase and is seen containing reaction vessels surrounded with ice to cool the water to the required experimental temperature.

2.5.3.2 Irradiance Levels

The range of exposure intensities were chosen according to monthly averaged irradiances on a horizontal surface at 77°S 166°E (McMurdo Station and Scott Base) and 43°S 172°E (Whakaraupo Harbour) [162]. The nine months of the year (August – April) where irradiances can be measured at McMurdo Station and Scott Base were divided into three seasons; spring (Aug, Sep, Oct), summer (Nov, Dec, Jan), and autumn (Feb, Mar, Apr). Solar irradiances were averaged over these three months. The average Antarctic spring and autumn irradiances are 130 W m^{-2} and 180 W m^{-2} respectively, however the solar simulator's lowest irradiance setting which could be reliably maintained was 330 W m^{-2}. The average monthly summer irradiance was approximately 650 Wm^{-2}. The middle value 500 W m^{-2} was chosen as a half-way point between these two values. For Whakaraupo Harbour, 160 W m^{-2} is the average monthly intensity over the months of May, June, and July. The average for August, September, and October is 340 W m^{-2}. The average for November, December, and January is 570 W m^{-2}. The average for February, March, and April is 390 W m^{-2} [162].

2.5.4 HPLC Analysis

Samples were analysed on an Agilent 1100 Series HPLC fitted with a photodiode array (PDA) detector, quaternary pump, mobile phase degasser, and autosampler. Aliquots of the test solutions were directly injected (40 μL) onto an Alltima C18 reverse phase column (250 x 4.6 mm ID, 5μm). Separation was carried out using a two-solvent isocratic gradient at ambient temperature and a flow rate of 1 mL min^{-1}, with a total run time of 20 minutes per sample. The isocratic gradient was set at 40% MQ water (0.1% formic acid) and 60% ACN. UV PDA detection was at 256 nm for mParaben, 228 nm for BPA, EE2, triclosan and OP, and 277 nm for BP-3. Retention times were as follows: mParaben (3.9 min), BPA (4.7 min), EE2 (5.3 min), BP-3 (10.2 min), triclosan (15.3 min), and 4-*t*-OP (18.1 min).

A six-point external standard calibration curve (0, 100, 200, 300, 400, and 500 μg L^{-1}) was prepared from the MQ working solution for each analysis run. The calibration standards were run before and after each batch of samples. The 300 μg L^{-1} standard and a MQ blank were analysed after every 12 samples to confirm the stability and reproducibility of the calibration. Calibration curves were linear (average $R^2 > 0.9741$, Table 2.7) over the calibration concentration range. The intra-day variability of the calibration curve slopes for all compounds was below 10%, except for 4-*t*-OP, which was 14.1%. The limit of detection (LOD) for each analyte was set to a signal-to-noise ratio of 3. The limit of quantification (LOQ) was set to signal-to-noise ration of 10.

Table 2.7: Summary of averaged calibration curve fits and slopes, %RSDs, LODs (μg L^{-1}), and LOQs (μg L^{-1}) of the six studied analytes.

Average	R^2	%RSD	Slope	%RSD	LOD	LOQ
mParaben	0.9989	0.2%	0.2045	1.9%	15	49
BPA	0.9978	0.4%	0.1272	1.3%	24	79
EE2	0.9944	0.7%	0.0339	3.1%	89	295
BP-3	0.9989	0.1%	0.0870	2.7%	17	58
Triclosan	0.9874	1.4%	0.0920	9.6%	33	109
OP	0.9741	2.5%	0.0529	14.1%	57	189

CHAPTER THREE

SOURCES AND TEMPORAL VARIATIONS OF MICROPOLLUTANTS IN WHAKARAUPO HARBOUR

3 Sources and Temporal Variations of Micropollutants in Whakaraupo Harbour

3.1 Introduction

The main sources of micropollutants into the environment are industrial and household sewage [3, 5, 6] and from washing off the skin during recreational activities [37-39]. Pollution of the marine environment caused by the release of sewage from WWTPs has become an important international topic [163]. The presence of micropollutants in coastal environments such as harbours, lagoons, estuaries, and bays has previously received only limited attention [164]. This scarcity of data for micropollutants in marine environments has been highlighted by a number of studies [50, 77, 82, 165]. The majority of environmental pollution research is mainly concerned with freshwater environments, and by comparison research on saline environments makes up just a small fraction of the available literature. The cause of this discrepancy has been speculated to arise from the assumption that the high dilution factors in marine environments reduces their potential environmental impact to negligible levels [77]. Another possible cause is the rising problem of freshwater scarcity, quality, and in particular the availability of clean drinking water sources.

Investigations of micropollutants in marine environments have to date focused primarily on harbours and bays containing large population centers and which receive large volumes of WWTP discharges such as in North America [164, 166], Europe [50, 77, 90, 167], and Asia [78, 79, 131, 168]. The marine environments of small countries or island nations such as New Zealand have to date been neglected. However there is little to suggest that these areas, where the majority of the population is located along the coast and therefore discharges its sewage into its coastal waters, are not equally affected by micropollutants. In the case of New Zealand up to 90% of all WWTP effluent is discharged into coastal waters, a large proportion of which receives little or no treatment [169]. Coastal habitats such as estuaries, coastal wetlands, coral reefs, and sea grass beds provide an important service to coastal marine health (i.e. nesting grounds, habitat etc) [152]. It is therefore important that the environmental risk of sewage discharges containing potentially endocrine disrupting compounds are properly assessed [170].

Environmental data for micropollutants in the New Zealand environment remains scarce. To address this data gap a multifaceted study was designed and implemented in which over 150 samples of treated wastewater effluent, receiving seawater, marine sediments, and green lipped mussels from Whakaraupo Harbour were collected over a one year period and

analyzed for a comprehensive suite of micropollutants representing a wide range of PCPs. Whakaraupo Harbour (Lyttelton Harbour) was an ideal study area as it receives municipal sewage discharges from three population centers, industrial discharges from a shipping port, and is a high-use recreational area, particularly during summer.

The goals of this study were to determine if micropollutants were being released into Whakaraupo Harbour, and if so, assess their distribution and the risks they potentially pose to the coastal ecosystem.

The specific objectives of this study were to:

- Indentify and quantify micropollutants within the effluents of the Lyttelton, Governors Bay, and Diamond Harbour WWTPs,
- determine how the concentration profiles of the target analytes vary between the three treatment plants over the course of a year,
- determine if micropollutants were present in the receiving coastal seawater and assess their variability across the four seasons,
- determine if micropollutants accumulate in sediments and aquatic biota living in the vicinity, and
- provide a preliminary assessment of the potential risk these micropollutants may pose to the New Zealand marine ecosystem.

3.2 Methods

The experimental methods used to extract the seawater, sediment, and mussel samples and their preparation for analysis are presented in Chapter 2.

3.2.1 Study Area

Lyttelton Harbour (Te Whakaraupo) is a marine inlet in Banks Peninsula located south of Christchurch along the east coast of the South Island of New Zealand. The three population centers located around the harbour are Lyttelton, Governors Bay, and Diamond Harbour (Figure 3.5). A major commercial shipping port is located in Lyttelton. Each of the three communities has its own WWTP (further details below) which discharge into Whakaraupo Harbour. All details on the treatment design and operational parameters observed throughout this study were obtained from the WWTP operator Kelvin Buckley or from Environment Canterbury reports on Whakaraupo Harbour [171, 172]. Each WWTP is based on the same engineering and treatment designs. Wastewater is treated via primary (screening) and

secondary treatment (extended aerobic aeration), followed by UV disinfection of the treated sewage effluent before being discharged into Whakaraupo Harbour. Sludge is regularly removed from the WWTPs and transported to the Bromley WWTP, which services the city of Christchurch. Hydraulic retention times (HRTs) of the three WWTPs were designed to be ~2 weeks. However in practice HRTs are reduced to several days, or as low as hours during heavy rainfall events. Physical parameters of the three WWTPs are summarized in Table 3.1. All demographic information presented below was sourced from the 2006 nationwide population census [173].

Table 3.1: Description of the physical parameters of the WWTPs in Lyttelton, Governors Bay, and Diamond Harbour [172].

WWTP	Population	Influent type	Average discharge *	Maximum permitted discharge
Lyttelton	3,000	Municipal/Industrial	750 m^3 d^{-1}	12,096 m^3 d^{-1}
Governors Bay	900	Municipal	150 m^3 d^{-1}	600 m^3 d^{-1}
Diamond Harbour	1,400	Municipal	200 m^3 d^{-1}	2,500 m^3 d^{-1}

* Data from January 2007 – June 2008

3.2.1.1 Whakaraupo Harbour

Whakaraupo Harbour was formed after the flooding of a crater of the now extinct volcano Mt Lyttelton ~2 million years ago. Today its basin is ~15 km long and 2 km wide, with an area of ~43 km^2 at mean low water springs (MLW). Large intertidal mudflats exist along the westerly and south-westerly coasts of the harbour by Governors Bay and Charteris Bay. During low tide these exposed mudflats have an area of ~11 km^2. The harbour bottom is rich in sediments, predominantly due to surface run-off from the surrounding catchment area. Yearly sediment accretion rates have been estimated at 44,300 tons per annum [171]. The major component of the eroding sediment is loess and loess colluvium material [174]. The potential for sediment inputs from Pegasus Bay (the coastal area of Canterbury, north of Banks Peninsula) has also been identified, but sediment volume influx is currently unknown [174]. However, the harbour entrance and the dredged shipping channel likely operate as efficient sinks for such materials, preventing any sedimentary material migrating southward downthe coast from being transported into the upper harbour [174]. Inshore sediments are a mix of gravel, sand, and shells, turning to muddier high silt/clay contents with increasing distance from the shore [175]. The organic content of the sediments is consistently low (<5% Ash Free Dry Weight), and there is little evidence of anoxic conditions throughout the harbour [175].

The tidal flux within Whakaraupo Harbour lies between 1 – 2 meters, giving rise to a large water exchange between tides within the harbour [175]. Mean tidal velocities decrease steadily as the tide enters the harbour, varying from 0.26 – 0.27 m s^{-1} at the harbour entrance in the east to 0.15 m s^{-1} at the western end of the harbour [174]. Occasionally a clockwise

gyre develops between the harbour entrance and the Lyttelton reclamation area during flood tide, with a comparable anti-clockwise gyre developing during ebb tide [174]. The average residence time of a unit of water inside the harbour is 2.09 days [174]. Despite its length ocean and wind swells can penetrate deep into the harbour, especially during northeaster winds, which can create significant water movement and sediment disturbance at shallow depths [176]. The water therefore has poor visibility (predominately zero-visibility), and a permanent layer of suspended solids floats over the surface of the bottom sediments [175].

The shipping lanes leading from the port to the harbour entrance are regularly dredged (>12 m below MLW) [176]. The port is also currently reclaiming 10 hectares of land on the eastern side using demolition rubble created from the February 2011 Earthquakes, which is pre-screened for any inappropriate materials such as asbestos before use [175].

Whakaraupo Harbour is a popular recreational site, especially during the summer months. A number of small beaches are located around the entire Whakaraupo Harbour area. Recreational boating and kayaking in the harbour is a common past time, and public marinas are located near Lyttelton, Governors Bay, and Diamond Harbour. Whakaraupo Harbour is also an important fishing and shellfish gathering area for local iwi.

3.2.1.2 Lyttelton

Lyttelton is the largest of the three communities situated around Whakaraupo Harbour, with ~1,300 households and a population of ~3,000. The WWTP (Figure 3.1) is located within the perimeter of the commercial port, and lies at the base of a steep rock cliff which provides shade for a large part of the morning. No other natural features surround the WWTP, which leaves it exposed to marine weather conditions. The sewage system of Lyttelton is a comprised of a combination of sewage canals and storm water drains, which leads to high in- and outflows during rain events. Large rain events have been known to cause overflows of the WWTP, as occurred in August 2012. Such large rain events are also known to wash out large proportions of the activated sludge used to treat the sewage, therefore affecting treatment efficiency. The WWTP treats the domestic waste of Lyttelton as well as the industrial waste of the port. The industrial component of the influent has also been identified to cause problems in the treatment efficiency of the WWTP. In July 2012 an unknown substance released from the port into the sewage system severely damaged the bacterial community within the WWTP. In addition, the infiltration of coal dust from the port into the WWTP has lead to excessive suspended solid loadings in the WWTP. Furthermore, due to its age a high level of leakage occurs within the Lyttelton sewage network.

Figure 3.1: Lyttelton WWTP.

3.2.1.3 Governors Bay

Governors Bay is the smallest of the three communities located alongside Whakaraupo Harbour, with ~300 households and a population of ~900. The WWTP lies in a relatively isolated location below Governors Bay along the coast. The WWTP (Figure 3.2) is surrounded by large amounts of vegetation and is therefore well shaded and sheltered from any severe weather. Governors Bay has the only sewage system with separate sewage and storm water drains, and therefore does not suffer from problems caused by large influxes of stormwater during rain events. All inflowing sewage is from domestic origin. However a chocolate processing facility located in Governors Bay disposes its waste via the sewage system, and was thought to have compromised the bacterial communities of the WWTP in 2012 (see Section 3.2.3 for more details).

Figure 3.2: Governors Bay WWTP, with aerators switched on.

3.2.1.4 Diamond Harbour

Diamond Harbour is situated on the southern site of Whakaraupo Harbour, directly opposite Lyttelton and the port, with ~580 households and a population of ~1,400. As in the case of Lyttelton the WWTP lies at the base of steep cliff below Diamond Harbour (Figure 3.3). It is extremely exposed to the marine environment, and receives both morning and afternoon sun. The sewage system of Diamond Harbour combines sewage canals and storm drains, and like Lyttelton the WWTP suffers from overflows and the washing out of sludge during large rain events such as occurred in August 2012. The outer holding tank was permanently covered in a thick layer of floating brown scum over the period of the study that was not observed at the other treatment plants. The reason for this is unknown.

Figure 3.3: Diamond Harbour WWTP (right) and an example of the UV disinfection lamp set-up (left) installed at all three WWTPs.

3.2.2 Sample Collection and Preparation

3.2.2.1 Sewage Effluent

The effluents of the three WWTPs were sampled on 11 separate occasions between January 2012 and January 2013. Samples were obtained between 8:30 – 10:30 AM on the first Monday or Tuesday of the month, with the exception of the December sampling round, which was carried out between 10 – 11:30 AM. The WWTPs were always sampled in the order of Lyttelton – Governors Bay – Diamond Harbour. Sewage samples (1 L) were collected as grab samples in duplicate directly into pre-washed 1 L amber bottles and were immediately acidified to pH 2 using concentrated sulphuric acid. The bottles were wrapped with bubble wrap, double bagged, and put on ice for transport back to the laboratory. Upon return to the

laboratory the samples were filtered separately through GF/C filter papers and extracted in the afternoon (~2 pm).

3.2.2.2 Seawater

Seawater sampling was carried out quarterly to span across the four seasons in April 2012, July 2012, October 2012, and January 2013. GPS coordinates for the seawater sampling sites are provided in Table 3.2. Samples were collected at low tide at 13 sites (Figure 3.5) around Whakaraupo Harbour and a separate reference site located in Pigeon Bay, a small and hydrologically separate marine inlet south of Whakaraupo Harbour. Three sampling sites in close proximity to the sewage outfalls of Lyttelton (Site 9), Governors Bay (Site 5), and Diamond Harbour (Site 7) were also selected. During the 4th sampling round in January 2013 a 14th site inside the shipping port was also sampled. In addition to these samples, an offshore seawater sample approximately 7 km of the coast of Banks Peninsula was collected during a separate boat trip in May 2012 for method validation purposes. Seawater samples (4 L) were collected from the boat as grab samples using a stainless steel bucket and transferred into pre-washed amber 4 L Winchester bottles, capped firmly, and transported back to the laboratory. The water samples were always collected before the sediment samples. Due to the large volumes of water that were sampled it was impractical to place the samples on ice. Upon return to the laboratory all samples were acidified to pH 2 using concentrated sulphuric acid before being stored overnight at 4°C. The seawater samples were filtered through GF/C filter papers the following day, and extracted the following day (within ~ 50 hours of sampling).

During the method development stages of this work, seawater was collected on six separate occasions in the same manner as described above from a pier close to sampling site two to provide seawater for spike recovery validation. Sampling in 2010 before the earthquakes occurred on the 3rd, 19th, and 30th of November. Sampling in 2011 after the earthquakes occurred on the 21st of September, and the 5th and 18th of October. This preliminary field study was completed to determine whether micropollutants were present in Whakaraupo Harbour before investing considerable resources into further fieldwork. Sample size of 4 L and 10 L were used to validate the SPE extraction efficiency. The 10 L sample sizes were included because this sampling size was used at some sites during the first Antarctic field trip (Chapter 4, Section 4.3.4.2), and to confirm if the reduced sample volume of 4 L was appropriate for the full field study.

3.2.2.3 Marine Sediments

Marine sediments were collected during the April and October sampling rounds from the same locations as the water samples using a stainless steel ponar grab sampler (16.5 cm x 15 cm). The sediment samples were always collected after the water samples. The samples were

transferred from the grab sampler into solvent rinsed 40 mL glass jars, capped firmly, and immediately placed on ice. Upon return to the laboratory the sediment samples were stored at -20°C until their extraction using ASE at Plant & Food Research Ruakura in Hamilton. Dry weights were determined for sediment samples before ASE, and are presented in Appendix A Table 8.9.

3.2.2.4 Green Lipped Mussels

Green lipped mussels (*Perna canalicula*) were obtained from five locations (Figure 3.6) in April 2012 (Battery Point, Rapaki, Sandy Bay, Port Levy, and Pigeon Bay), and from four locations in January 2013 (Battery Point, Sandy Bay, Port Levy, and Pigeon Bay). The mussels were to be originally collected in October 2012, however bad weather conditions hindered access to some sites. Mussels were not collected from the Rapaki site in January 2013 due to low mussel numbers. The mussels were kept on ice during transport to the laboratory, where they were kept at 4°C until processing. The mussels were shucked within at most 72 hours of collection. During processing the mussels were cleaned and weighed before dissection, and the mussel tissue and shell weights were recorded for each mussel after dissection. A total of eight mussels were combined into a composite sample for each site and homogenised before being stored at -20°C until their extraction using ASE at Plant & Food Research Ruakura in Hamilton. Dry weights were determined for each composite mussel sample before extraction. The dry weights and mussel tissue weights used for each composite are presented in Appendix A Table 8.10.

Table 3.2: Harbour depth and GPS coordinates for all seawater and sediment sampling sites.

Site	1	2	3	4	5
Harbour Depth	1.3 m	1.6 m	2.1 m	3.1 m	3.5 m
GPS Coordinates	S 43° 38.744’	S 43° 38.844’	S 43° 37.562’	S 43° 36.667’	S 43° 37.276’
	E 172° 40.424’	E 172° 42.036’	E 172° 39.532’	E 172° 40.614’	E 172° 40.453’
Site	6	7	8	9	10
Harbour Depth	5.5 m	5.0 m	7.5 m	8.0 m	4.2 m
GPS Coordinates	S 43° 37.065’	S 43° 37.483’	S 43° 37.389’	S 43° 36.530’	S 43° 37.681’
	E 172° 42.001’	E 172° 43.045’	E 172° 44.035’	E 172° 44.026	E 172° 44.904’
Site	11	12	13	14	Pigeon Bay
Harbour Depth	9.6 m	13.2 m	15.4 m		4.2 m
GPS Coordinates	S 43° 36.604’	S 43° 36.238’	S 43° 35.849’	S 43° 36.483’	S 43° 40.617’
	E 172° 45.366’	E 172° 47.157’	E 172° 49.149’	E 172° 43.088’	E 172° 53.879’

3.2.3 Observed Impacts on the Wastewater Treatment Plants

A treatment plant can over the course of its operating lifetime be exposed to a variety of external influences which can affect its treatment efficiency. Such events can be of natural origin such as the yearly fluctuations of temperature, or heavy rain events in cases where the sewer systems are not separated from storm water drains. Other events are of human origin,

such as chemical spills. Over the course of this study a number of such events occurred and were observed to impact all three WWTPs. This section gives an overview of these field observations.

May: The pH levels in Lyttelton and Governors Bay were too low, and lime was added to raise the pH back to a normal operating range of neutral pH. The cause of the pH change in Lyttelton was unknown. According to Kelvin Buckley the origin of the pH change in Governors Bay was a chocolate processing facility that recently came into operation.

June: A clogged drain in the township of Lyttelton meant the maintenance company had to pump sewage directly into the plant. Furthermore Governors Bay continued to experience problems with its treatment. During the weekend preceeding sampling the activated sludge at Governors Bay unexpectedly dislodged itself, turning the whole oxidation pond into a brown foamy slurry with the look and consistency of a dirty chocolate drink. Kelvin Buckley continued to attribute this effect to the chocolate processing facility, and took steps to inform the owners of their likely impacts.

July: An unknown chemical spill in the shipping port in Lyttelton entered the WWTP, causing a severe microbial die-off from which the WWTP would take until well into August to recover. Governors Bay appeared to have returned to normal function after the management of wastes from the chocolate processing facility were addressed.

August: Lyttelon had not fully recovered from the bacterial die-off experienced the previous month. Furthermore, excessive rains the week before sampling caused much of the activated sludge to be flushed out of the Lyttelton and Diamond Harbour WWTPs and into the harbour. A similar rain event occurred several weeks later.

October: The aerators at Lyttelton were accidentally left turned on the night before sampling. In addition to the effect of warming temperatures with the onset of spring the extra oxygen is likely to have caused increasing microbial activity which dislodged much of the activated sludge. Heavy rains also flushed out the activated sludge in the Lyttelton and Diamond Harbour WWTPs a few weeks prior to sampling.

3.2.4 QA/QC

All QA/QC procedures used during sampling, sample preparation, and analysis are described in full in Chapter 2.

3.3 Results and Discussion

3.3.1 Statistical Analysis

All data were stored and edited for statistical analysis in Excel (2008 for Mac, Version 12.1.0). All statistical analyses were performed in R (Version 2.14.1 for Mac). Both Excel and R were used to prepare graphics. Statistical analyses of the sewage data were only undertaken for analytes which were detected in at least seven of the eleven sampling rounds (OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, E1, and Cstanol). All duplicate measurements were averaged before being included in the statistical analysis of the data. All detected analytes were measured above the limit of quantification. Correlations between analytes within each WWTP were determined using the Pearson's Product-Momentum Correlation test. One-way ANCOVA, where the ways were the WWTPs and adjusted for month, was used to determine whether each analyte's concentration profile differs between WWTPs.

Fourier transform spectral analysis for time series data was used to determine whether any analyte concentrations exhibited seasonality trends (i.e. increasing concentrations in winter compared to summer or vice versa). The data of each analyte were fitted using a basic linear model and compared against a linear model containing one set of Fourier harmonics using a F-test of the two nested models.

For the seawater data statistical analyses were only performed on analytes detected in at least 50% of samples (mParaben, 4-MBC, BP-3, BPA, OMC, and E1). Results for duplicate samples were averaged prior to statistical analysis. For analytes detected below the LOQ a value of half the LOQ was used in the analyses. Differences between sampling rounds were analyzed using a paired student t-test. Correlations between analyte concentrations and site distance from the entrance harbour were determined using the Pearson's Product-Momentum Correlation test.

3.3.2 Analytical Method Performance

All surrogate recoveries were quantified against the comparative standard. Detailed recovery data of all sewage surrogate and analyte spike recoveries are provided in Appendix A. Surrogate recoveries for the duplicate sewage sample (Appendix A Table 8.3) were always in close agreement for each month (~7% difference or less, but occasionally up to ~20%), and were also close in value between each WWTP, but varied between months. Some of this variability was likely due to SPE extraction variability. However $^{13}C_6$-mParaben, $^{13}C_6$-NP, and $^{13}C_{12}$-triclosan appeared to be relatively susceptible to matrix effects during GC-MS analysis, which would have significantly contributed to the recovery variability. Standard deviations of the recoveries averaged over the whole sampling period were therefore

relatively high, ranging between 16.0% and 29.5% for $^{13}C_{12}$-BPA and $^{13}C_6$-mParaben respectively. Average recoveries (mean ± 95% confidence interval, n = 66) were 106.6% ± 7.3%, 99.4% ± 4.8%, 81.1% ± 6.7%, 106.6% ± 6.9%, 83.0% ± 3.9%, and 89.3% ± 4.7% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 respectively. These recovery values are consistently high across all samples and meant the concentrations of detected analytes were not corrected against surrogate recovery. The sewage effluent surrogate recoveries were slightly elevated compared to the 1 L MQ water recoveries determined during method validation (Chapter 2, Table 2.2b), except for $^{13}C_{12}$-BPA, which were lower in the sewage, and $^{13}C_6$-E2 which did not change. The observed surrogate recovery elevation was likely due to matrix enhancement effects arising from the presence of co-extracted matrix components originating from the sewage effluent. The recoveries of the target analytes spiked into sewage effluent samples (Appendix A Table 8.4) behaved in a similar way to the surrogates. Recoveries varied between months and mostly remained within an acceptable range of 80 – 120 %. However, signs of matrix enhancements were occasionally observed. The quality assurance field blank, MQ water, SPE cartridge, sodium sulfate, and solvent blanks demonstrated minor signs of background contamination for mParaben, OP, BP-3, BPA, and OMC. Background concentrations of the SPE cartridge blank were used to correct all sewage data by subtraction before being reported.

The seawater surrogate and analyte spike recoveries were comparable for those obtained for the sewage effluent. Detailed recovery data of all sewage surrogate and target analyte spike recoveries from the seawater samples are provided in Appendix A Table 8.5 and Table 8.6. Recoveries were in excellent agreement between each sampling site for each of the four sampling rounds, but varied between sampling rounds. However this between-rounds variability was generally lower than that observed for the recovery of the surrogate spike recoveries of the sewage effluent samples. The recovery variability was highest for $^{13}C_6$-mParaben and $^{13}C_{12}$-triclosan recoveries. These recoveries were enhanced in the third and fourth sampling round compared to the first and second. Average recoveries (mean ± 95% confidence interval, n = 65) were 92.9% ± 7.9%, 85.0% ± 2.5%, 57.9% ± 2.6%, 107.0% ± 6.4%, 79.6% ± 2.8%, and 88.6% ± 3.1% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 respectively. These mean recoveries fall within <1 – 14% of the mean recoveries determined from the method development samples (Chapter 2, Table 2.2b). Recoveries of $^{13}C_6$-mParaben were slightly higher (~11%) and $^{13}C_{12}$-BPA were slightly lower (~14%) than those determined during method development. As with the sewage results the seawater results were not corrected for recovery. Furthermore, blank controls again showed only occasionally minor signs of background contamination for mParaben, OP, BP-3,

BPA, and BPA. Background concentrations of the cartridge blank were used to correct all seawater data by subtraction before being reported.

Marine sediment surrogate recoveries were more variable than those from the sewage effluent or seawater. This variability was also observed during method validation. Detailed recovery data of sediment analyte and surrogate spike recoveries from the April and October samples are provided in Appendix A Table 8.7 and Table 8.8. Surrogate recoveries were equally variable for the April and October samples. Average recoveries (mean ± 95% confidence interval, n = 35) were 87.4% ± 10.1%, 79.6% ± 8.5%, 83.3% ± 7.3%, 88.4% ± 5.0%, 81.9% ± 5.5%, and 73.9% ± 4.0% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 respectively. Blank controls (extraction thimble blank, water blank, solvent blanks) showed minor signs of background contamination for mParaben, OP, 4-MBC, BP-3, BPA, and OMC. However, the thimble blanks of the April samples showed elevated contamination of OMC, while the thimble and water blanks of the October samples showed elevated BPA contamination. All data were corrected for background contamination from the ASE thimble blanks.

Matrix interferences from mussels collected at the Lyttelton field sites were greater than those determined in the reference mussels, which were described in Chapter 2. This is most likely due to site difference rather than seasonal differences because the reference mussels and second round of Whakaraupo Harbour mussels were both collected in summer 2013, yet exhibited different degrees of matrix interference. Detailed recovery data have been provided in Appendix A Table 8.11. Only the surrogates $^{13}C_6$-mParaben, $^{13}C_6$-bParaben and $^{13}C_6$-E2 could be recovered, and acceptable spike recoveries were only achieved for mParaben, eParaben, OP, pParaben, BP-3, E2, EE2, and E3. Only limited environmental information could therefore be discerned from these biota samples.

3.3.3 Preliminary Study

A total of ten analytes were detected over the course of the six preliminary sampling rounds (Table 3.3) designed to provide preliminary seawater data and seawater for method validation purposes. Detailed data on individual analyte concentrations and surrogate recoveries are provided in Appendix A Table 8.1. The detected analytes were also regularly detected during the subsequent comprehensive harbour sampling study, except for triclosan. Triclosan was only detected in the 10 L samples of the preliminary study, and never in the 4 L samples, most likely due to the larger concentration factor. Results and literature comparisons of the complete harbour seawater data are described in more detail in Section 3.3.5.

Table 3.3: Concentrations of target analytes detected at a single site (Charteris Bay, close to sampling site 2) in Whakaraupo Harbour from six different sampling occasions in spring 2010 and 2011.

Analyte	Range (ng L^{-1})	Frequency	Literature range (ng L^{-1})	Reference
mParaben	1.2 – 9.3	6/6	2.1 – 62	[50]
pParaben	1.5 – 5	3/6	0.5 – 7.9	[50]
4-MBC	<3.2 – 5.7	4/6	13.1 – 798.7	[39, 70]
BP-3	<2.6 – 11	6/6	1.8 – 3300	[38, 70, 71]
Triclosan	0.5 – 1	2/6	0.008 – 99.3	[62, 73, 74, 164, 177, 178]
BP-1	<0.8	1/6	280	[71]
BPA	3.1 – 9.7	5/6	<0.08 – 2470	[50, 77-79, 82, 90, 131, 167, 168, 179, 180]
OMC	<1.9 – 3.9	2/6	7.4 – 389.9	[39, 70]
E1	<7.0	2/6	0.08 – 103.9	[77, 82, 90, 168, 179, 181]
E3	<2.1	2/6	ND	[77, 82, 164]

ND = not detected
< = Chromatograph peak identifiable as target analyte, but corresponding concentration below the limit of quantification as identified in Table 2.1.

3.3.4 WWTP Effluent Concentrations

The effluents of each WWTP were found to contain a very similar range of analytes. The range and frequency of detected analytes for each WWTP are presented in Table 3.4, along with a comparison to literature concentration ranges. The complete data are provided in Appendix A Table 8.2, all surrogate recoveries in Appendix A Table 8.3, and target analyte spike recoveries in Appendix A Table 8.4. Despite all three WWTPs using the same treatment system, and being located in the same harbour, distinct concentration patterns of target analytes could be observed in the treated effluents. These observations highlight the varied and complicated nature of wastewater treatment. The observed patterns and differences will be the main focus of discussion for the sewage effluent section of this chapter.

The analytes detected in all WWTP effluent samples were OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, E1, and Cstanol. Less frequently detected analytes were mParaben, eParaben, pParaben, bParaben, E2, EE2, and E3. pParaben was only detected once in effluent from Diamond Harbour, and EE2 was only detected once in Lyttelton. bParaben and E2 were only detected once in Lyttelton and Diamond Harbour, E3 was detected twice in Lyttelton and on five occasions in Diamond Harbour. All of the detected analytes were present at concentration ranges comparable to international data (Table 3.4). However, while all parabens were detected at least once, internationally they are usually detected much more frequently, and at higher concentrations between <0.2 – 423 ng L^{-1} [46-51, 53]. Similarly, OMC was not detected in any sewage samples, but is commonly detected in overseas WWTP effluents between <10 – 177 ng L^{-1} [56-58]. Up to 90% of OMC has been estimated to adhere

to suspended influent organic matter [56]. Dissolved OMC could therefore have been completely removed during the treatment processes in the three WWTPs. Poor extraction efficiencies can be ruled out as the paraben and OMC spikes were always adequately recovered from the effluents (Appendix A Table 8.4). It may indeed be the case that these three WWTPs can very effectively remove paraben preservatives and OMC from wastewater influents. However, influent samples were not sampled in this study, so the removal efficiencies for these micropollutants cannot be confirmed.

The variety of detected target analytes and the differences of their detection frequency and concentration ranges in the WWTP effluents is consistent with reports in the research literature, with the exception of the paraben preservatives. In contrast to the limited detection of parabens in the WWTP effluents of this study, a study of eight WWTPs in Canada frequently detected paraben preservatives in the treated effluent, in particular mParaben and pParaben (<10 – 50 ng L^{-1} and <10 – 40 ng L^{-1} respectively) [51]. In comparison, a Spanish study from Catalonia infrequently detected paraben preservatives in the sewage effluents [59]. In the Whakaraupo study the UV filters 4-MBC, BP-3, and BP-1 were detected in all WWTP effluent samples. A study of five WWTPs across Spain measured 4-MBC and BP-3 at levels (42 – 326 ng L^{-1} and 42 – 260 ng L^{-1} respectively) comparable to the data from the present study, but only 50% and 80% of the time respectively [58]. However, this study also detected OMC (16 – 177 ng L^{-1}) in 65% of samples [58]. This analyte was not detected in any of the effluent samples of the Whakaraupo study.

BP-3 and BP-1 were detected in all effluent samples from the Whakaraupo WWTPs, and at concentrations (11 – 207.3 ng L^{-1} and 3.6 – 146.2 ng L^{-1} BP-3 and BP-1 respectively) up to four-fold higher than those measured in urban WWTP effluents in Santiago de Compostela, Spain [61]. The Santiago study reported the systematic presence of the UV filters BP-3 and BP-1 in sewage influent (216 – 462 ng L^{-1} and 131 – 245 ng L^{-1} respectively) [61]. However, these UV filters were reported to be effectively removed during the treatment process to below the detection limit in at least 50% of effluent samples (<LOD – 44 ng L^{-1} and <LOD – 41 ng L^{-1} for BP-3 and BP-1 respectively) [61].

Triclosan was similarly detected in all Whakaraupo WWTP effluent samples (Table 3.4), which compares well to the 95% detection frequency in five WWTPs across Spain [58]. However the Whakaraupo WWTP effluent concentration range was lower (13.1 – 121.5 ng L^{-1}) compared to the Spanish effluents (60 – 719 ng L^{-1}). In contrast, triclosan was not detected in the effluents from the Catalonian study [59]. mTriclosan was also frequently detected in the Whakaraupo effluents ranging between 2.7 – 35.3 ng L^{-1}, but its detection frequency was lower than that for triclosan. Internationally mTriclosan is also commonly detected in

wastewater effluents between <2 – 50 ng L^{-1}, and at a lower frequency than its parent compound triclosan [63, 64].

E1 was the most commonly detected estrogenic steroid hormone in the Whakaraupo effluent samples, ranging between 2.1 – 113.8 ng L^{-1}. In comparison, E2, EE2, and E3 were detected infrequently, but at similar concentrations to previously reported studies (Table 3.4). E1, E2, and EE2 are commonly detected in WWTP effluents worldwide, and often occur together [67]. The removal efficiencies of steroid hormones during wastewater treatment can be close to 100% [182]. However this removal efficiency can vary between WWTPs, and can range from almost complete removal to virtually no removal [182]. Differences in operating temperature, HRTs, and differences in the conjugated fractions of steroid hormones have been postulated as the cause [182]. These treatment differences have been previously observed in New Zealand, where a survey of steroid hormones in the sewage effluents of three WWTPs showed different patterns of E1, E2, and EE2 between each WWTPs [183].

Table 3.4: Data summary of detected analytes, frequency of detection, detected concentration range, and comparisons to international ranges.

Analyte	WWTP	Frequency	Concentration range (ng L^{-1})	Literature range (ng L^{-1})	Reference
mParaben	Lyttelton	4/11	1.0 – 3.6	2.1 – 423	[47-49]
	Governors	1/11	2.0		
	Diamond	3/11	0.9 – 21.2		
eParaben	Lyttelton	1/11	4.0	<0.3 – 69	[47, 49, 50]
	Governors	1/11	6.5		
	Diamond	1/11	6.8		
OP	Lyttelton	10/11	4.7 – 205.8	3.7 – 3,949	[49-51]
	Governors	10/11	3 – 11.4		
	Diamond	10/11	4.2 – 22.4		
pParaben	Lyttelton	0/11	–	<0.5 – 95	[47, 49, 184]
	Governors	0/11	–		
	Diamond	1/11	49.2		
bParaben	Lyttelton	1/11	5.9	<0.2 – 83	[46, 47, 50, 51]
	Governors	0/11	–		
	Diamond	1/11	7.8		
NP	Lyttelton	0/11	–	<29 – 3,210	[47, 50, 51]
	Governors	0/11	–		
	Diamond	0/11	–		
4-MBC	Lyttelton	11/11	23.2 – 210.4	42 – 2300	[56, 58]
	Governors	11/11	54.1 – 155.4		
	Diamond	11/11	63.8 – 428.8		
BP-3	Lyttelton	11/11	11.0 – 164.8	3 – 2,196	[49, 55, 56]
	Governors	11/11	22.8 – 89.3		
	Diamond	11/11	22.8 – 207.3		
mTric	Lyttelton	9/11	2.7 – 35.3	<2 – 51	[63, 64]
	Governors	7/11	3.6 – 12.3		
	Diamond	9/11	5.2 – 15.2		
Triclosan	Lyttelton	11/11	13.1 – 121.5	0.4 – 1120	[54, 185, 186]
	Governors	11/11	13.8 – 56.1		
	Diamond	11/11	16.7 – 108.6		
BP-1	Lyttelton	11/11	3.6 – 61. 2	<2 – 41	[49, 59, 61]
	Governors	11/11	6.7 – 19.6		
	Diamond	11/11	18.6 – 146.2		
BPA	Lyttelton	10/11	3.7 – 165.3	1.3 – 2600	[47, 51, 53]
	Governors	11/11	3.5 – 69.9		

OMC	Diamond	11/11	5.7 – 63.4	<10 – 177	[56-58]
	Lyttelton	0/11	–		
	Governors	0/11	–		
E1	Diamond	0/11	–	<0.1 – 147	[51, 54, 66, 67]
	Lyttelton	9/11	2.4 – 78.4		
	Governors	9/11	2.1 – 62.7		
E2	Diamond	9/11	4.0 – 113.8	0.2 – 158	[66]
	Lyttelton	1/11	18.8		
	Governors	0/11	–		
EE2	Diamond	3/11	1.3 – 7.0	<0.3 – 7.5	[65]
	Lyttelton	1/11	13.1		
	Governors	0/11	–		
E3	Diamond	0/11	–	<0.3 – 275	[54, 66, 187]
	Lyttelton	2/11	<0.6 – 11.3		
	Governors	0/11	–		
Cstanol	Diamond	5/11	1.1 – 8.9	10 – 200,000	[188]
	Lyttelton	11/11	10.6 – 867.1		
	Governors	11/11	15.7 – 459.6		
	Diamond	11/11	49.7 – 315.7		

3.3.4.1 WWTP Analyte and Concentration Differences

The concentrations of the most commonly detected analytes OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, E1, and Cstanol from each WWTPs are graphically illustrated in Figure 3.4. To show whether concentration ranges differed between treatment plants and whether analytes exhibited signs of seasonality (discussed in more detail in Section 3.3.4.2) their significance *p*-values have been added. The value p_{diff} indicates the differences between each WWTP pair, while p_{season} represents seasonality trends. Significance p_{diff} values have been tabulated in Table 3.5.

Table 3.5: Summary of p_{diff}-values indicating where concentration profiles of specific analytes significantly differ between WWTP.

WWTP Pair	OP	4-MBC	BP-3	Triclosan	mTric	BP-1	BPA	E1	Cstanol
Lyttelton:Governors	0.028*	0.673	0.474	0.490	0.176	0.657	0.0920^	0.781	0.347
Lyttelton:Diamond	0.043*	0.0194*	0.012*	0.983	0.6072	0.00029***	0.091^	0.718	0.925
Governors:Diamond	0.839	0.0495*	0.0019**	0.503	0.372	0.000085***	0.991	0.932	0.396

p-value, ^ <0.1, * <0.05, ** <0.01, ***<0.001

The concentrations of OP measured in the Lyttelton WWTP effluents were consistently many times greater than for Governors Bay and Diamond Harbour ($p < 0.05$). OP concentrations between Governors Bay and Diamond Harbour were not statistically different. Similarly, BPA concentrations in Lyttelton were consistently two times higher than those measured in Governors Bay and Diamond Harbour during winter and spring, although the difference is only weakly significant ($p_{diff} < 0.10$). These differences of OP and BPA concentrations between the WWTPs is illustrated in Figure 3.4. These observations are consistent with BPA and OP being commonly used industrial chemicals, and the Lyttelton WWTP receiving industrial sewage from the shipping port, as well as municipal waste from incoming ships.

A second striking difference between the WWTPs was that the concentration range of the UV filters 4-MBC, BP-3, and BP-1 were significantly higher ($p < 0.05 – 0.000085$ depending on the UV filter) in the Diamond Harbour effluents compared to Lyttelton or Governors Bay. Furthermore, 4-MBC effluent concentrations were higher than those of BP-3 and BP-1 in all three WWTPs. Higher 4-MBC concentrations than BP-3 concentrations have been reported previously in overseas studies [56, 57]. The UV filters concentrations in Diamond Harbour were statistically higher throughout the year than at the other two WWTPs. This pattern suggests the Diamond Harbour WWTPP receives wastewater with a different UV filter composition than the Lyttelton or Governors Bay WWTPs, and may also indicate different usage patterns of PCPs containing UV filters. The Diamond Harbour WWTP may also be less effective at removing UV filters during treatment. Diamond Harbour is a popular site for holiday homes. This may lead to higher UV filter loadings in the sewage influent due the increased use of sunscreens by vacationing families in summer. However this does not fully explain the permanently increased effluent UV filter concentrations throughout the year. The concentration ranges and patterns of triclosan, methyl triclosan, BPA, E1, and Cstanol in the three WWTPs effluents displayed no statistically differences.

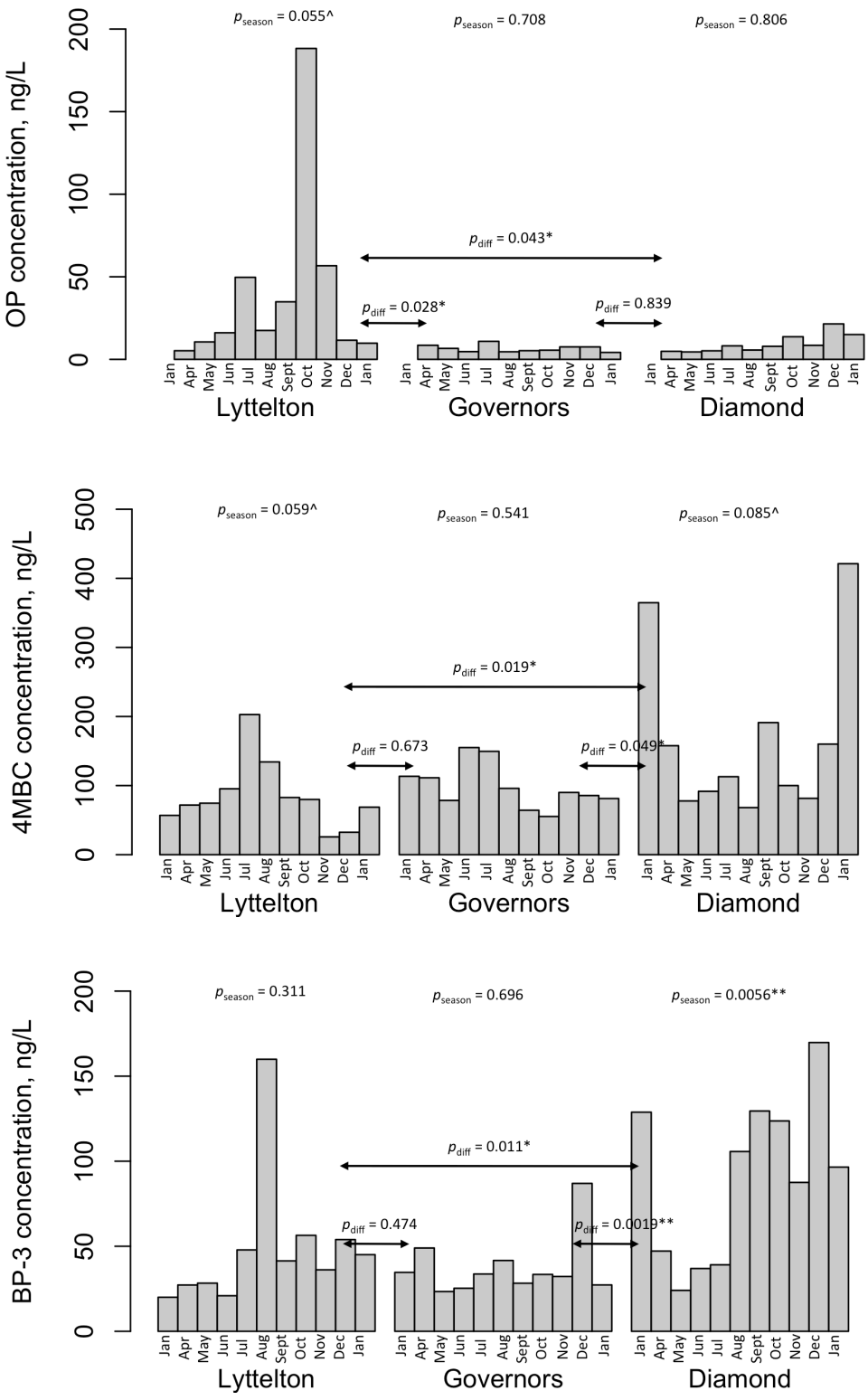


Figure 3.4: Average monthly analyte concentrations (ng L^{-1}) of the most frequently detected analytes OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, E1, and Cstanol in the WWTP effluents of Lyttelton, Governors Bay, and Diamond Harbour. p_{diff} indicates concentration differences between WWTPs. p_{season} indicates the presences of a seasonality trend.

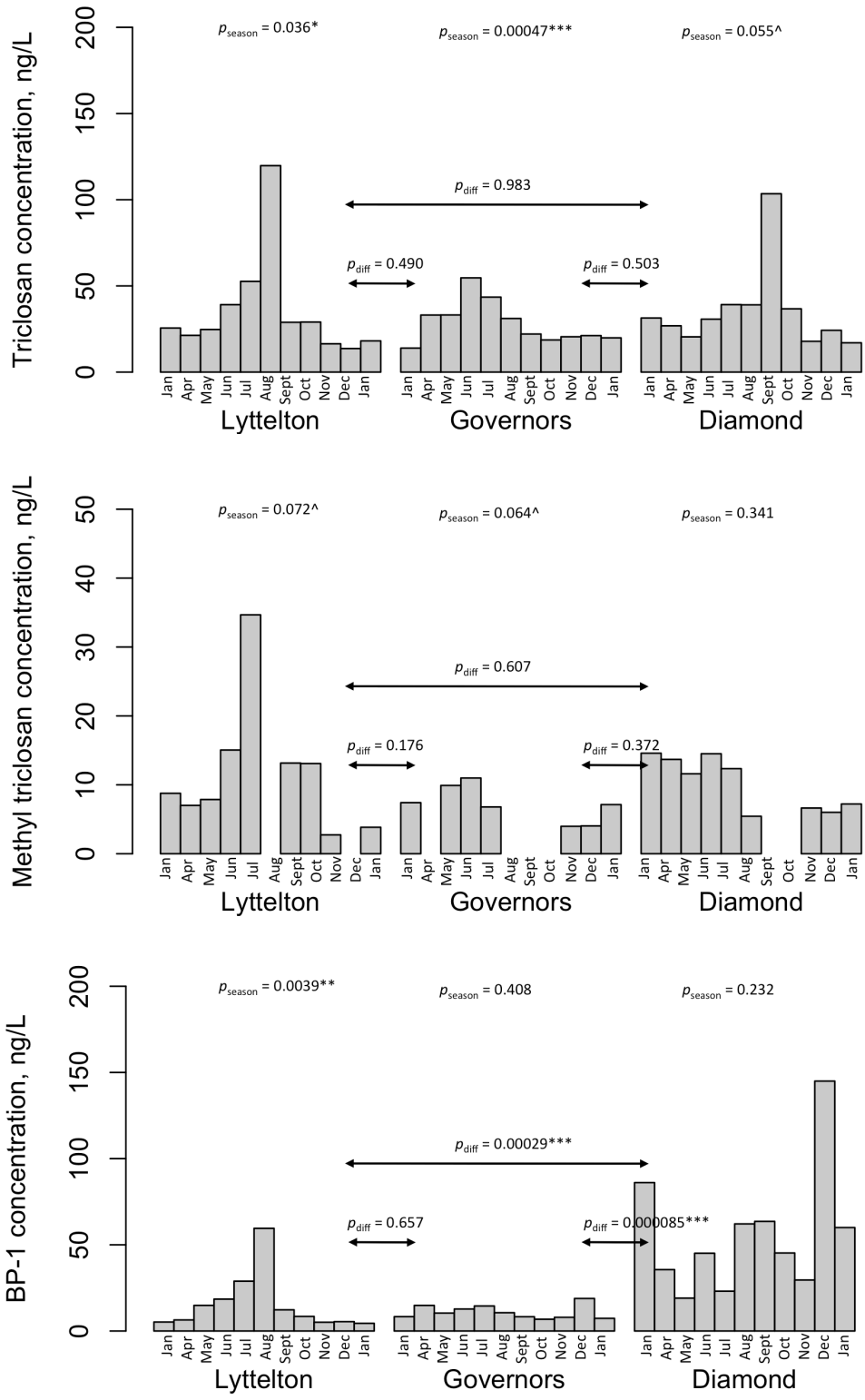


Figure 3.4 cont: Average monthly analyte concentrations (ng L^{-1}) of the most frequently detected analytes OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, E1, and Cstanol in the WWTP effluents of Lyttelton, Governors Bay, and Diamond Harbour. p_{diff} indicates concentration differences between WWTPs. p_{season} indicates the presences of a seasonality trend.

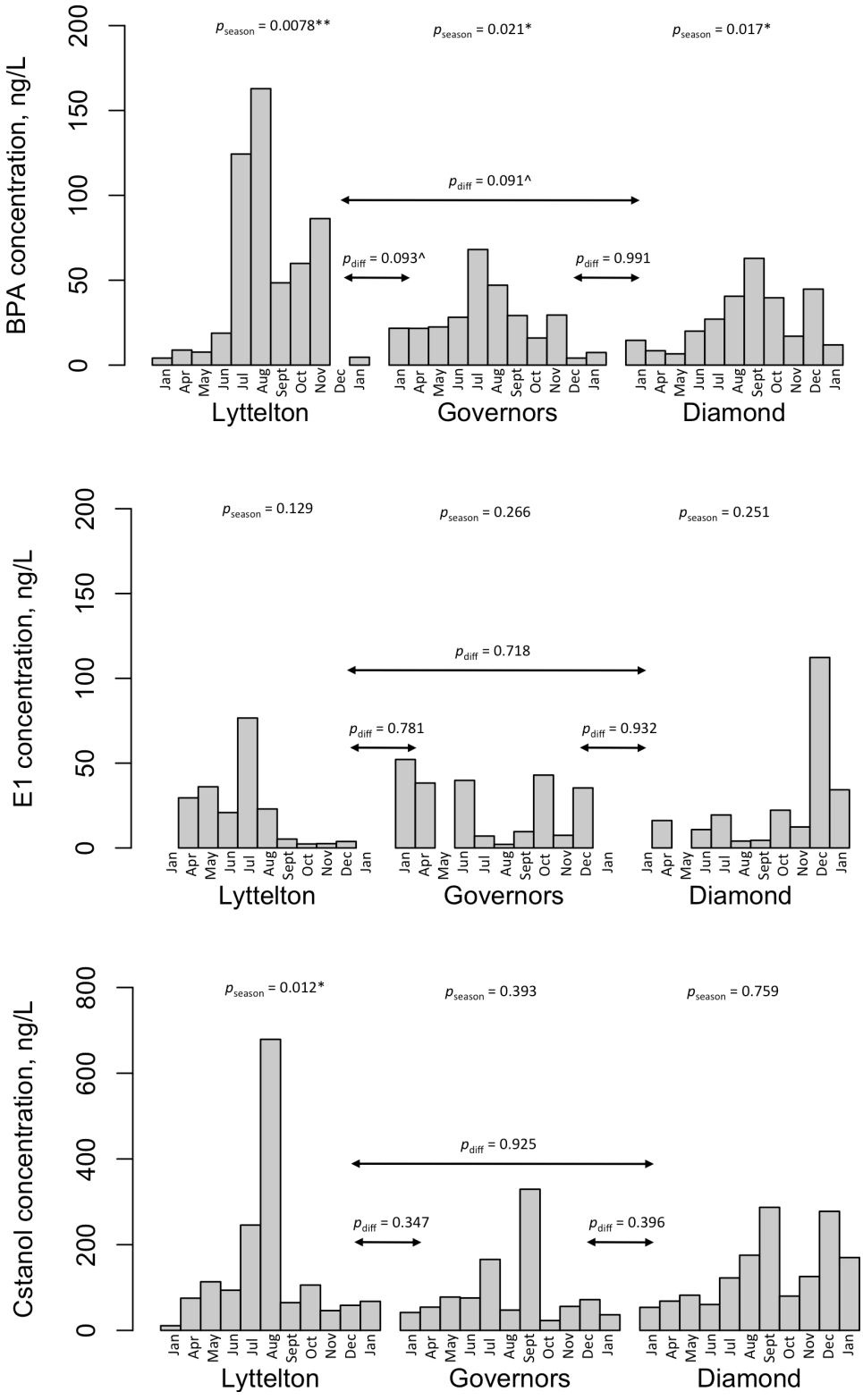


Figure 3.4 cont: Average monthly analyte concentrations (ng L^{-1}) of the most frequently detected analytes OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, E1, and Cstanol in the WWTP effluents of Lyttelton, Governors Bay, and Diamond Harbour. p_{diff} indicates concentration differences between WWTPs. p_{season} indicates the presences of a seasonality trend.

As an indication of the degree to which the treatment efficiency/influx of micropollutants into each WWTP fluctuated across the year the concentrations of each analyte were correlated against one another. Strong positive correlations indicate analyte concentrations rise and fall concurrently throughout the year, and would be an indicator of a similar rise and fall of influent inputs and/or change in treatment efficiency. Pearson correlation coefficients between each combination of analytes, and their significance values are tabulated in Table 3.6. Correlations significant at $p < 0.1$ or lower have been tabulated, but only correlations at $p < 0.05$ are discussed. Pearson correlations ranged from relatively weak ($R = 0.5939$, $p < 0.05$) to very strong ($R = 0.9829$, $p < 0.001$). Analyte concentrations were also correlated against ambient air temperatures (Section 3.3.4.2)

The detected analytes correlated to various degrees with each other within each WWTP. The only correlation shared by all WWTPs was that between BP-3 and its metabolite BP-1 ($p < 0.01$ for all WWTPs). Interestingly, a similar correlation between triclosan and its metabolite methyl triclosan was not observed. Of the three WWTPs the analyte concentrations within the Lyttelton WWTP shared the most correlations between each other. This indicates the conditions inside the Lyttelton WWTP were the least variable. While OP did not correlate with any other analyte or temperature 4-MBC correlated with all analytes except OP and BP-3. In Governors Bay only two analyte-analyte correlations were observed, between 4-MBC and triclosan ($p < 0.01$), and between BP-3 and BP-1, ($p < 0.01$). This demonstrates most analyte concentrations fluctuate independently of each other in the Governors Bay WWTP, and possibly indicates variable influent loadings and complex environmental conditions inside the WWTP. Diamond Harbour displayed the second most analyte correlations of the three WWTPs. However the Diamond Harbour correlation profile was different to that of Lyttelton and Governors Bay. While in Lyttelton and Governors Bay all correlations were positive, a negative correlation between BP-3 and methyl triclosan ($R = -0.6188$, $p < 0.05$), between BPA and methyl triclosan ($R = -0.7619$, $p < 0.01$) and between Cstanol and methyl triclosan ($R = -0.6332$, $p < 0.05$) was observed in Diamond Harbour. This indicates that influent loadings and/or the environmental conditions inside the Diamond Harbour WWTP follow a different pattern compared to the Lyttelton and Governors Bay WWTPs. It may also be an indicator of a different population demographic in Diamond Harbour due to the high number of holiday homes. These contrasting results for three WWTPs of similar design highlights the complexity of sewage treatment processes, and makes it difficult to predict the treatment efficiencies for organic micropollutants between treatment plants.

Table 3.6: Pearson correlation coefficients for statistically significant correlations between the concentrations of the most commonly detected analytes in Lyttelton, Governors Bay, and Diamond Harbour and between measured ambient temperatures.

Lyttelton	**OP**	**4-MBC**	**BP-3**	**Triclosan**	**mTric**	**BP-1**	**BPA**	**E1**	**Cstanol**
OP	1								
4-MBC		1							
BP-3			1						
Triclosan		0.637*	0.876***	1					
mTric		0.749**			1				
BP-1		0.689*	0.842**	0.983***		1			
BPA		0.641*	0.739**	0.797**		0.800**	1		
E1		0.824**			0.718*			1	
Cstanol		0.594^	0.931***	0.975***		0.972***	0.803**		1
T_1		-0.721*			-0.709*		-0.671*	-0.716*	
T_2		-0.583^					-0.574^	-0.663*	
T_3		-0.782**		-0.620*	-0.594^	-0.694*	-0.730*	-0.759**	-0.574^
Governors	**OP**	**4-MBC**	**BP-3**	**Triclosan**	**mTric**	**BP-1**	**BPA**	**E1**	**Cstanol**
OP	1								
4-MBC		1							
BP-3			1						
Triclosan		0.753**		1					
mTric					1				
BP-1			0.741**			1			
BPA							1		
E1								1	
Cstanol									1
T_1				-0.637*			-0.857***		
T_2							-0.847**		
T_3							-0.915***		
Diamond	**OP**	**4-MBC**	**BP-3**	**Triclosan**	**mTric**	**BP-1**	**BPA**	**E1**	**Cstanol**
OP	1								
4-MBC		1							
BP-3			1						
Triclosan				1					
mTric			-0.619*		1				
BP-1			0.825**			1			
BPA			0.636*	0.766**	-0.762**		1		
E1	0.864***					0.753**		1	
Cstanol	0.599^		0.615*		-0.633*		0.753**		1
T_1		0.673*	0.610*			0.728*			
T_2	0.756**		0.620*			0.656*		0.708*	
T_3		0.638*				0.598^			

p-value, ^ <0.1, * <0.05, ** <0.01, ***<0.001

3.3.4.2 Temporal Analyte Concentration Trends

The concentration patterns of most analytes over time were different between at least one of the three WWTPs. Only the concentrations of triclosan and BPA did not differ statistically in the effluents of the three WWTPs. Statistical significance values p_{season} are added to Figure 3.4,

and have also been tabulated in Table 3.7. For simplicity the observed trends are discussed separately for each WWTP before comparisons to the literature are made.

Table 3.7: Summary of p_{season}-values indicating where the temporal concentration changes of each analytes show statistically significant signs of seasonality.

WWTP	OP	4-MBC	BP-3	Triclosan	mTric	BP-1	BPA	E1	Cstanol
Lyttelton	0.055^	0.059^	0.311	0.036*	0.072^	0.0039**	0.0078**	0.129	0.012*
Governors	0.708	0.541	0.696	0.00047***	0.064^	0.408	0.021*	0.266	0.393
Diamond	0.806	0.085^	0.0056**	0.055^	0.341	0.232	0.017*	0.251	0.759

p-value, ^ <0.1, * <0.05, ** <0.01, ***<0.001

Lyttelton WWTP effluent:

Concentrations of OP, 4-MBC, triclosan, methyl triclosan, BP-1, BPA, and Cstanol were generally higher in the colder winter/spring months than the warmer summer/autumn months. The gradual concentration increase leading into winter, and the gradual decrease leading into summer suggests the treatment efficiency of these analytes is seasonally dependant ($p < 0.1$ for OP, 4-MBC, and methyl triclosan, and $p < 0.05$ for triclosan and Cstanol, and $p < 0.001$ for BP-1 and BPA, Figure 3.4). Maximum effluent concentrations of each analyte were reached in the winter months of June, July, or August. While BP-3 and E1 showed no such gradual temporal variations their maximum concentration also occurred in July and August respectively. E1 was not detected in January 2012 and January 2013, and E1 concentrations were higher in autumn and winter than spring and summer. Longer term monitoring may reveal E1 and possibly BP-3 are also seasonally dependant.

The concentration of OP notably peaked in October. The likely reason for this however was the fact that the aerators were accidentally switched on overnight, possibly causing an increase in microbial activity, which were able to degrade the source of OP, the alkylphenol ethoxylates, more effectively. EE2 was only detected in the July effluent samples, and was also only one of two times in which E3 was detected. A spike in the OP concentration also occurred in July. This may be related to a chemical spill which leaked into the Lyttelton WWTP, as mentioned in Section 3.2.3. Following the large rain event in August a spike in the concentrations of BP-3, triclosan, BPA, BP-1, and Cstane were observed. This was also one of only two times when mTriclosan was not detected in the Lyttelton WWTP effluent. These micropollutant concentration spikes stand out clearly in the August sample in Figure 3.4, and were most likely caused by the rain event flushing out the activated sludge of the WWTP. This provides evidence of the importance of activated sludge on the treatment efficiency of micropollutants within WWTPs. In comparison the flushing out of the activated sludge in Diamond Harbour WWTP did not produce any micropollutant concentration spikes.

Governors Bay WWTP effluent:

Temporal concentration trends were only observed for triclosan (p = 0.00047), methyl triclosan (p = 0.064), and BPA (p = 0.021). Similar to the observations in the Lyttelton WWTP the Governors Bay concentrations of triclosan and BPA were higher in the winter months, with maximum concentrations reached in June and July respectively. Methyl triclosan was not detected in April, August, September, and October. The concentrations of OP and BP-1 remained relatively constant, while those for 4-MBC, BP-3, E1, and Cstanol fluctuated throughout the study period and did not demonstrate any specific trends or correlations.

Diamond Harbour WWTP effluent:

Detected analytes in Diamond Harbour were found to follow temporal trends that were both unique to each analyte, and to the micropollutant concentrations measured in Lyttelton and Governors Bay (Figure 3.4). Triclosan and BPA concentrations increased in winter and spring compared to summer and autumn (p = 0.055 and 0.017 respectively), however maximum concentrations for both analytes occurred in September instead of June, July or, August, as was the case in Lyttelton and Governors Bay. OP concentrations remained relatively constant, while BP-1, E1, and Cstanol fluctuated throughout the study period. There was no sign of a temporal trend for methyl triclosan, and was not detected in September and October. The temporal trends of 4-MBC and BP-3 were different to all other observed trends. Concentrations of 4-MBC were higher in summer than winter (p = 0.085), the only such observed trend. This may be related to the presence of holiday homes in Diamond Harbour, which when used in summer would lead to a higher input of UV filters into the WWTP by vacationing families. Concentrations of BP-3 were relatively constant throughout most of winter, spring, and summer, with a decrease during parts of autumn and winter. This suggests the annual concentration cycle observed for these two analytes has shifted by several months in Diamond Harbour compared to the other two WWTPs.

The effects of temperature on analyte concentrations in the three WWTP effluents was investigated. Air temperatures measured by the NIWA weather station [189] located in Lyttelton were used as neither air nor water temperatures at the three WWTPs are monitored. Analyte concentrations of the WWTP effluents were compared against three different temperature records (Table 3.6). T_1 is the temperature recorded at 8 AM on the day of sampling. To take into account the effect the previous days weather may have on a WTTP (e.g. a hot day may buffer against the effects of a cold day the day after) the maximum temperature recorded the previous day has been selected as T_2. Extending this reasoning the average of the maximum temperature of the previous three days has been selected as T_3. Correlations significant at $p < 0.1$ were tabulated, but only correlations at $p < 0.05$ are

discussed. As was observed for the analyte-analyte correlations, the majority of analyte-temperature correlations were observed for the Lyttelton WWTP. With the exception of OP and BP-3 all analyte concentrations correlated negatively with T_3, with analyte concentrations increasing with decreasing air temperatures. With the exception of OP, which did not correlate with air temperature, and E1 which did not exhibit a seasonal trend, analytes with statistically significant temperature correlations also exhibited a statistically significant seasonal trend.

In Governors Bay, only triclosan and BPA showed negative correlations with ambient air temperatures. These analytes were also the only analytes that exhibited a significant seasonal trend with concentration. In contrast, in Diamond Harbour all the observed analyte-temperature correlations were positive, with concentrations decreasing with decreasing air temperature. All three UV filters measured in Diamond Harbour correlated positively with T_1. As suggested earlier, the use of holiday homes may be the cause for these observed differences in UV filter concentrations and patterns. These holiday homes would be used more frequently during warmer weather than cold weather, leading to a positive correlation of UV filter concentrations with air temperature. Overall the number of analyte-temperature correlations was approximately equal for the three different temperature data sets.

These analyte and WWTP specific concentration trends make it difficult for comparisons to international data to be made. The fact that each of the three WWTPs is located in the same geographical area and utilizes the same treatment design, yet still yields varying and sometimes opposing data trends, leads to the conclusion that we still do not understand the interplay between WWTP design, population demographics, and other environmental factors. The observed concentration differences between the Lyttelton, Governors Bay, and Diamond Harbour WWTPs suggests such trends may not only be controlled by seasonal effects such as temperature, but may also be controlled by factors unique to each WWTP (i.e. location, population demographic, weather exposure, etc).

Most of the observed temporal trends in the Whakaraupo study show increasing concentration in winter compared to summer for OP, 4-MBC, triclosan, methyl triclosan, BP-1, BPA, and Cstanol in at least one of the three WWTPs. Only limited previous studies are available with long-term monthly sampling regimes to allow for detailed comparisons with this study. The majority of previous studies have reported increasing concentrations of these micropollutants in summer rather than winter [57, 59, 190, 191]. Increases in organic micropollutant concentrations in effluents during winter compared to summer are usually attributed to decreasing microbial activity in winter, and have been observed for E1 and E3 [190], triclosan [164], and various pharmaceuticals [192, 193]. Conversely, elevated effluent concentrations

in summer compared to winter are usually attributed to an increased use of consumer products, and have been observed for 4-MBC, BP-3, OMC, NP, OP, and triclosan [57, 59, 190, 191]. Temporal or seasonal trends may therefore depend on the balance between winter temperatures, seasonally changing consumer product usage, and the compound in question.

The UV filter concentrations measured in the three Whakaraupo Harbour WWTP effluents demonstrated only few seasonal trends. In the Lyttelton WWTP effluents only 4-MBC and BP-1 concentrations increased in winter compared to summer. In contrast, 4-MBC concentrations in Diamond Harbour increased in summer compared to winter. Lastly, BP-3 in Diamond Harbour was lower in autumn compared to the other three seasons, with BP-3 concentrations being lower than those of 4-MBC. In a northern China WWTP the influent and effluent concentrations of the UV filters 4-MBC, BP-3, and OMC were also found to vary with season. However, contrary to the Whakaraupo study the concentrations of UV filter increased in summer (July and September) compared to winter (February) [57]. Similarly a Spanish study observed effluent BP-3 concentrations varied between months, with concentrations at 20 ng L^{-1} in May, 100 ng L^{-1} in September, and falling below the detection limit in January [59]. A Swiss study of WWTP effluents saw no seasonal increases in UV filter concentrations [56]. However UV filter concentrations were elevated in the influent in June compared to April [56]. Similarly, a US study observed increased influent concentrations of BP-3 in summer compared to winter, but saw no seasonal differences in the effluent concentrations of BP-3 and pParaben [53].

Triclosan concentrations in all three WWTPs increased in winter compared to summer, and exhibited a similar range in concentration between all three WWTPs. A similar seasonal pattern has also been observed in a South Carolina study of two WWTPs, and has been linked to reduced temperatures [164]. Furthermore, the concentrations of triclosan between the two studied WWTPs were also approximately equal [164]. In contrast, two US studies observed no triclosan concentration increases in the effluents during summer [53, 191]. Concentrations of the microbial metabolite methyl triclosan in Lyttelton were higher during colder months compared to warmer months. In Governors Bay however concentrations of methyl triclosan were generally lower or below the detection limit in the colder months. The cause for this discrepancy remains unidentified, and requires further investigation. No previously published literature on the seasonal fluctuations of methyl triclosan in sewage effluents was available for comparison.

The concentrations of BPA increased in winter compared to summer in all three WWTP effluents. The concentrations of OP however did so only in Lyttelton. Previous overseas investigations of the concentrations of BPA in WWTP effluents also showed no seasonal

trend [53, 190]. Increasing effluent concentrations of OP were however previously observed in summer compared to winter [190].

No seasonal changes were observed for the steroid hormones in the Whakaraupo study, with E1 the most frequently detected steroid hormone, followed by E3. Other international studies have demonstrated dissimilar trends to this study, and to each other. The concentrations of E1 and E3 were elevated in winter compared to summer, and E2 displayed little seasonal variation in Chinese WWTP effluents [190]. E1 showed WWTP specific behaviour in South Carolina, as it was consistently fully removed in the effluents of one WWTP, but not the second WWTP [164]. E3 was not detected in any of the South Carolina effluents [164]. Lastly, an Italian study measured E1, E2, E3, and EE2 in six Italian WWTPs over five months [187]. Similarly to the Whakaraupo study, E1 and E3 were the most abundant estrogens [187].

3.3.5 Whakaraupo Harbour Seawater

Micropollutants were detected in all seawater samples collected from Whakaraupo Harbour, and the Pigeon Bay reference site. The results from each of the four sampling rounds are summarized in Table 3.8, together with comparative data from previously published studies on micropollutants in seawater. The data are also summarized in Figure 3.5. The complete data are provided in Appendix A Table 8.5, including analyte spike recoveries (Appendix A Table 8.5) and surrogate spike recoveries (Appendix A Table 8.6). The most commonly detected analytes (at least 50% of samples) in the seawater were mParaben, 4-MBC, BP-3, OMC, BPA, and E1. Less frequently detected analytes were OP, pParaben, bParaben, BP-1, E2, E3, and Cstanol. All detected concentrations were low compared to the literature ranges reported for overseas marine environments (Table 3.8). This is most likely due to reduced population levels within the Whakaraupo harbour catchment compared to the locations of the other study areas, and the well-flushed nature of Whakaraupo Harbour. Despite the frequent detection of OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, E1, and Cstanol in the sewage effluents entering the harbour, only 4-MBC, BP-3, BPA, and E1 were observed to persist in the seawater. The remaining analytes may either degrade (bio- or photodegradation), associate with suspended particulates and sediments, or be taken up by marine biota within the harbour. For example, triclosan and OP are known to readily photodegrade [116, 194, 195] or associate to particulate matter [186] and sediments [62, 196, 197]. Similarly, methyl triclosan readily associates to sediments [196] and can bioaccumulate [62], but is more resistant to photodegradation than triclosan [62, 63, 99].

Despite the limited detection of mParaben in the sewage effluents, and absence of OMC, these analytes were regularly detected in the seawaters from Whakaraupo Harbour and Pigeon Bay. The QA/QC blanks indicated only occasional minor background contamination by

mParaben and OMC, which was conservatively subtracted from the environmental data before being reported. Similar results have been obtained by a Spanish study which detected OMC at a higher frequency in river waters (83%) than in the sewage effluents (65%) [58]. Sewage leaks have been reported in the Lyttelton sewage system, and could be a possible source of these compounds. However, a seawater sample collected at Site 14 (Figure 3.5) inside the Lyttelton port, during the January 2013 sampling round showed no elevated concentrations of target analytes, including mParaben and OMC. The paints on the hulls of boats and ships may be a second potential source. The presence of alkylphenols in the marine environment around Singapore has for example been attributed to boat traffic [131]. However sites 10 and 14, the locations of two popular marinas in Whakaraupo harbour, also showed no signs of elevated concentrations of target analytes.

mParaben could possibly be released into the harbour as glucuronide or sulfonate conjugates which are subsequently cleaved. Parabens also readily react with free chloride and bromide, and these halogenated derivatives can reach concentrations comparable to those of their parent compounds within the WWTP [198]. These halogenated paraben derivatives have been detected in Japanese rivers [199]. It is plausible upon release into the environment these halogenated parabens are photodegraded back to their parent compound. However to date there is no evidence to support this theory. In the case of OMC there are no –OH or –COOH groups available for conjugation, and halogenation reactions have to date not been reported to occur with OMC.

One possible point source of mParaben and OMC in the sampled seawaters is the Christchurch sewage outfall into Pegasus Bay, located three kilometers directly offshore the city. A sample collected downstream from this outfall, approximately 7 km offshore from the Whakaraupo harbour entrance also contained mParaben, BP-3, BPA, and OMC at similar levels to those detected inside Whakaraupo harbour (Appendix A Table 8.5). A second source could be recreational activities, which have been shown to increase UV filter concentrations in recreational bodies of water in summer [39]. Recreational sources of UV filters to bodies of water requires further study, but has been postulated to be important in areas of limited water exchange, such as fjords or lakes [39], but potentially not in bodies of water with high water exchange such as Whakaraupo harbour. While an increase in OMC was observed in January, OMC was still detected in the waters of Whakaraupo harbour throughout the year. Furthermore, a similar disparity between sewage effluent and seawater levels of mParaben and OMC was observed in the Antarctic case study (Chapter 4, Section 4.3.4). This suggests there may be an unknown environmental transport mechanism for mParaben and/or OMC. This discrepancy, plus the detection of analytes in the offshore and at Pigeon Bay suggest there may also be additional as yet unidentified source of micropollutants.

Table 3.8: Data summary of analytes detected in seawater (ng L^{-1}) and marine sediments (ng g^{-1} dry weight) from each individual sampling round, with comparisons to data from international marine environments [a].

		Seawater			Marine Sediments		
Analyte	**Month**	**Range (Frequency)**	**Literature Range**	**Reference**	**Range (Frequency)**	**Literature Range**	**Reference**
mParaben	April	<0.8 – 1.2 (14/14)	2.1 – 62	[50]	0.7 – 1.7 (2/14)	NA	NA
	July	<0.8 – 2.7 (13/14)			–		
	October	<0.8 – 1.5 (14/14)			<0.2 – 0.4 (11/14)		
	January	<0.8 – 9.4 (10/15)			–		
eParaben	April	ND	<0.3 – 15	[50]	ND	NA	NA
	July	ND			–		
	October	ND			ND		
	January	ND			–		
OP	April	<0.2 – 0.5 (3/14)	<0.04 – 800	[50, 77-79]	0.2 – 2.5 (12/14)	<0.7 – 1700	[78, 163, 200-203]
	July	ND			–		
	October	0.3 – 0.8 (3/14)			0.5 – 0.6 (2/14)		
	January	0.6 – 0.8 (2/15)			–		
pParaben	April	ND	<0.5 – 7.9	[50]	ND	NA	NA
	July	1.7 (1/14)			–		
	October	ND			ND		
	January	<0.8 – 2.2 (4/15)			–		
bParaben	April	<0.5 – 0.8 (2/14)	<0.2 – 7.1	[50]	ND	NA	NA
	July	0.9 (1/14)			–		
	October	ND			ND		
	January	ND			–		
NP	April	ND	20.2 – 269	[50, 77-79, 82, 179, 204]	ND	2.2 – 4560	[78, 82, 163, 165, 168, 203-205]
	July	ND	<0.5 - 755		–		
	October	ND			ND		
	January	ND			–		
4-MBC	April	5.1 (1/14)	13.1 – 798.7	[39, 70]	ND	NA	NA
	July	<3.2 – 3.4 (4/14)			–		
	October	<3.2 – 3.4 (14/14)			1.6 – 4.3 (4/14)		
	January	<3.2 – 6.4 (14/15)			–		
BP-3	April	<2.6 – 7.3 (5/14)	1.8 – 3300	[38, 70, 71]	<0.8 – 1.6 (9/14)	0.272 – 4.66	[206, 207]
	July	<2.6 – 3.7 (14/14)			–		
	October	<2.6 – 3.2 (14/14)			<0.8 (3/14)		
	January	<2.6 – 6.3 (15/15)			–		
mTric	April	ND	NA	NA	ND	2.0 – 11.4	[196]
	July	ND			–		
	October	ND			ND		
	January	ND			–		
Triclosan	April	ND	0.008 – 99.3	[62, 73, 74, 164, 177, 178]	ND	183.5 – 0.27	[165, 166, 185, 196, 208]
	July	ND			–		
	October	ND			ND		
	January	ND			–		
BP-1	April	1.3 – 3.3 (2/14)	280	[71]	0.4 – 1.3 (6/14)	0.259 – 0.607	[206]
	July	ND			–		
	October	ND			ND		
	January	<0.8 (1/15)			–		
BPA	April	<1.3 – 4.9 (14/14)	<0.08 – 2470	[50, 77-79, 82, 90, 131, 167, 168, 179, 180]	<0.4 – 7.1 (12/14)	<0.09 – 160	[78, 82, 163, 168, 180, 202, 203, 205, 208]
	July	<1.3 – 5.2 (14/14)			–		
	October	<1.3 – 2.9 (3/14)			1.8 – 9.9 (1/14)		
	January	1.7 – 2.2 (2/15)			–		
OMC	April	<1.9 – 6.7 (9/14)	7.4 – 389.9	[39, 70]	0.8 – 2.8 (7/14)	1.6 – 9	[209]
	July	<1.9 – 4.5 (9/14)			–		
	October	<1.9 – 2.6 (14/14)			<0.6 – 11.5 (9/14)		

	January	<1.9 – 4.1 (14/15)			–		
E1	April	<7.0 (4/14)	0.08 – 103.9	[77, 82, 90, 168, 179, 181]	ND	<0.1 – 10.3	[168, 203, 207, 208]
	July	ND			–		
	October	<7.0 (14/14)			<2.0 (13/14)		
	January	<7.0 (15/15)			–		
E2	April	ND	0.4 – 175	[82, 168, 179, 180]	ND	<0.1 – 4.8	[168, 180, 203, 207, 208]
	July	<0.4 (2/14)			–		
	October	ND			ND		
	January	<0.4 (4/15)			–		
EE2	April	ND	0.14 – 101.9	[77, 82, 90, 179, 180]	ND	<0.28 - 41	[82, 180, 208]
	July	ND			–		
	October	ND			ND		
	January	ND			–		
E3	April	ND	ND	[77, 82, 164]	0.6 (1)	ND	[82, 205]
	July	<2.1 (1/14)			–		
	October	ND			ND		
	January	ND			–		
Cstanol	April	ND	<10 – 47,500	[210]	2.6 – 18.7 (14/14)	<10 – 47,500	[210]
	July	2.4 – 5.4 (3/14)			–		
	October	0.4 – 6.8 (2/14)			2.0 – 98.7 (14/14)		
	January	ND			–		

ND = not detected
NA = no reference data available
[a] Marine environment was defined to include coastal, lagoon, harbour, bay, estuary, and tidal areas.

3.3.5.1 Spatial Differences

Only occasional and minor differences were observed in the presence and concentrations of micropollutants in Whakaraupo Harbour seawater between sampling sites. Trends were difficult to establish due to analyte concentrations being close to the detection limits. In April mParaben concentrations correlated with distance to the harbour entrance, and increased with proximity to the harbour entrance ($p = 0.0055$). In July and January the concentrations of 4-MBC and OMC followed the opposite trend ($p = 0.0518$ and $p = 0.0278$ respectively). The concentrations of the less frequently detected analytes were generally evenly distributed along the length of the harbour. However in April 4-MBC was only detected at Site 7 (5.1 ng L^{-1}), the Diamond Harbour outfall, while BPA was highest at the Lyttelton outfall, Site 9 (4.9 ng L^{-1}). OP and Cstanol were also most frequently detected at Site 9. OP was detected in April (0.5 ng L^{-1}) and October (0.8 ng L^{-1}), while Cstanol was detected in July (2.8 ng L^{-1}) and October (6.8 ng L^{-1}). Furthermore, in July Cstanol was detected at three locations, all of which were at or next to the sewage outfalls (at Site 9/Lyttelton and Site 5/Governors Bay, and Site 8 next to Diamond Harbour).

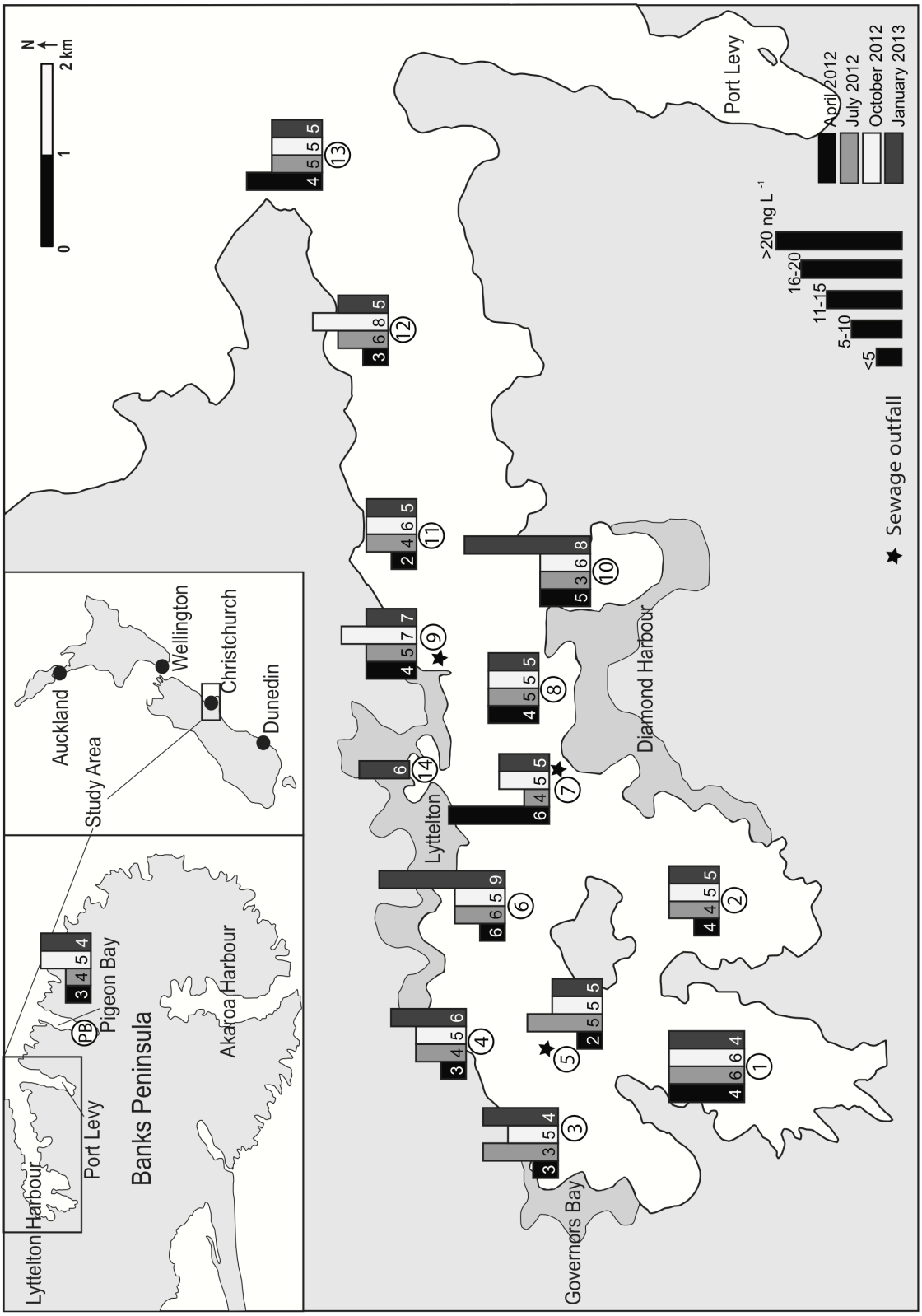


Figure 3.5: Whakaraupo study area and distribution of detected target analytes in seawater at each sampling location. Sampling locations are indicated by the circled numbers. The height of each bar shows the total concentration burden of micropollutants (ng L^{-1}) at each site for each of the four sampling rounds (distinguished by colour). The number inside each bar indicates the number of detected target analytes.

The absence of spatial trends for micropollutants in Whakaraupo Harbour is consistent with international studies of micropollutants in coastal marine waters. These studies have demonstrated higher rates of micropollutant detection and concentrations at coastal sites with riverine inputs or in manmade marine canals [164, 179], and within coastal water bodies with restricted flows or water exhange [164, 170, 179, 211]. Conversely, reduced frequencies of detection and concentrations of micropollutants have been measured within marine areas with high rates of mixing and large tidal flows [164, 170, 179, 201, 211].

3.3.5.2 Seasonal Differences

Seasonal changes were difficult to determine due to the low seawater concentrations in Whakaraupo Harbour. However, micropollutant concentrations in the seawater tended to be elevated during the warmer months of October and January. This is the opposite seasonal concentration trend to that observed in the WWTPs. Concentrations of mParaben in seawater were slightly higher in October (p = 0.0497) and January (p = 0.0828) compared to July. Concentrations of 4-MBC were also higher in October and January compared to April and July ($p < 0.05$). Concentrations of OMC generally did not vary between seasons, except for a slight increase in January over October (p = 0.0487). Lastly, E1 was detected more frequently in October and January compared to April and July (p = 0.00007). The concentration of BP-3 showed no correlations to seasonal changes.

Limited seasonal trends have also been observed internationally. The UV filters 4-MBC, BP-3, and OMC were detected more than twice as frequently along a Norwegian coastal zone, including several recreational beaches, in July compared to May the proceeding year before recreational water activities resumed [39]. Maximum concentrations of the UV filters (798.7 ng L^{-1} 4-MBC, 439.9 ng L^{-1} BP-3, and 389.9 ng L^{-1} OMC) were measured in water adjacent to recreational beaches located in sheltered low water exchange areas. UV filter concentrations in less sheltered areas were reduced [39]. In a study displaying a distinct seasonal trend the concentration of OMC in a Swiss river system was higher in summer compared to winter [83].

The concentrations of BPA in the waters of Whakaraupo Harbour were higher in the autumn/winter season (April and July) compared to the spring/summer season (October and January)($p < 0.05$), and overall highest in July ($p < 0.05$). However, a study on its presence in the Dutch freshwater, estuarine, and marine environment did not observe seasonal changes in concentration [212]. In addition, a New Orleans study of BPA and triclosan only measured concentration increases during storm water events. This increase was thought to have originated from non-point source sewage contamination associated with the aging New Orleans sewer system [88].

3.3.5.3 Potential Role of Photochemical Degradation

Photochemical degradation is potentially a significant removal mechanism of micropollutants in the environment [151]. Previous studies have demonstrated a range of micropollutants can undergo photodegradation, including pharmaceuticals [160], BPA [213], natural and synthetic steroid hormones (e.g. EE2) [214], NP [215], OP [194], triclosan [195], organic UV filters [216], phthalates [217, 218], and paraben preservatives [115]. Micropollutants such as BPA, EE2, and UV filters have been shown to be relatively resistant to photochemical degradation processes [213, 216, 219, 220]. Other micropollutants such as triclosan and OP however have been shown to readily photodegrade [62, 221]. This resistance to photodegradation may explain the persistent occurrence of BPA, E1, and UV filters, and the absence of triclosan and OP, in Whakaraupo Harbour. Photodegradation mechanism are expected to be reduced during winter when light levels are low. However, the observed seasonal trends tended to show increased seawater concentrations of the photo-stable target analytes in summer compared to winter. Photo-stable micropollutants may therefore remain unaffected by light conditions even in summer, while photo-sensitive micropollutants may be sensitive enough to readily degrade even under reduced winter light conditions. The role of photochemical degradation in the fate and behavior of mParaben, BPA, EE2, BP-3, triclosan, and OP in the marine environment is investigated and discussed in more detail in Chapter 5.

3.3.6 Marine Sediments

All marine sediment samples, including those from the Pigeon Bay reference site, contained detectable levels of micropollutants. However the composition and concentration profile of the target analytes over the two sampling rounds was extremely different. The results from the two sampling rounds are presented in Table 3.8, including detection frequency, concentration ranges, along with a comparison to literature ranges. The data are also summarized in Figure 3.6. The complete data are provided in Appendix A Table 8.7, with analyte spike recoveries and surrogate recoveries are provided in Appendix A Table 8.7 and Table 8.8 respectively. Dry weight percentages of the marine sediments are provided in Appendix A Table 8.9.

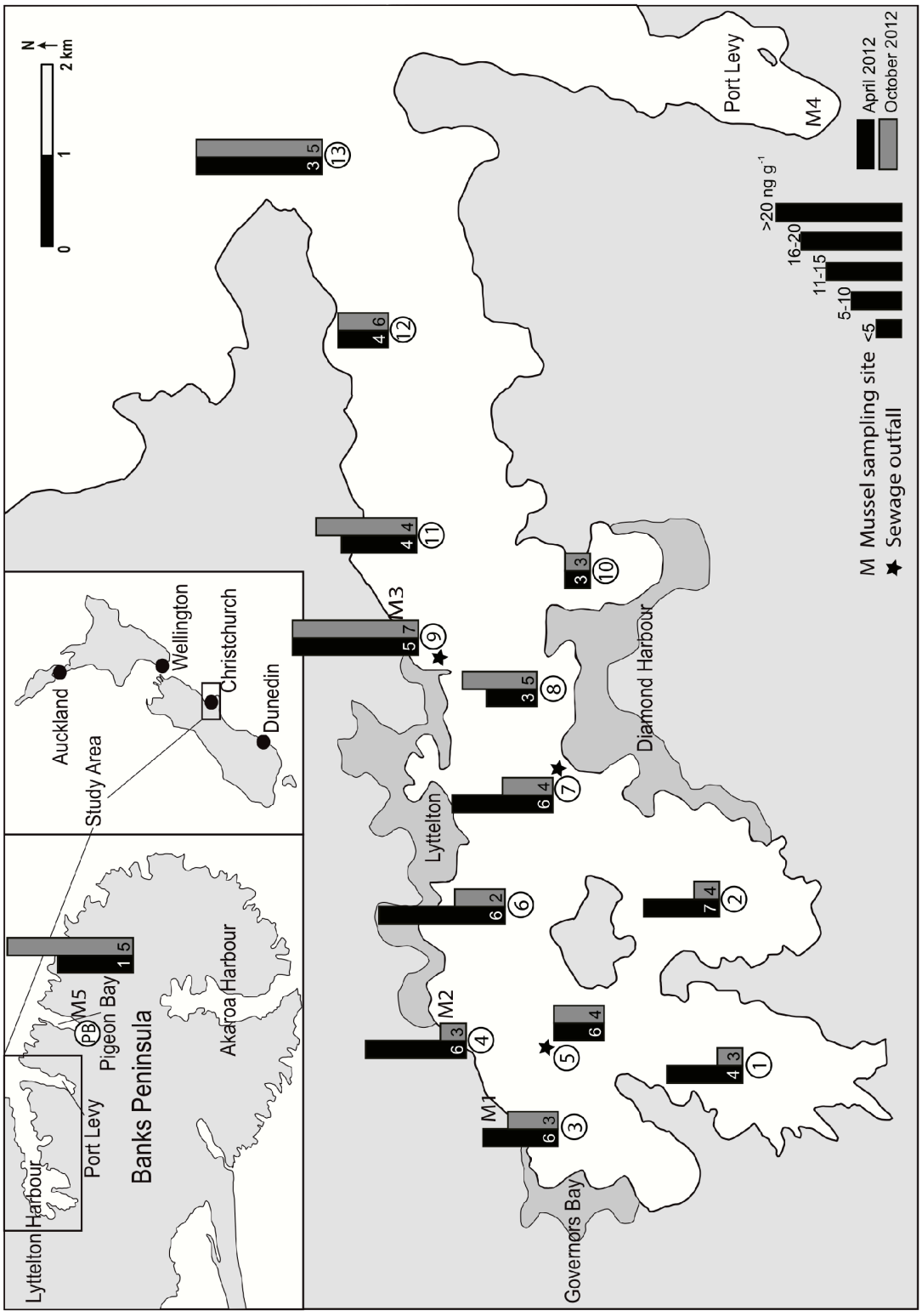


Figure 3.6: Whakaraupo study area and distribution of detected target analytes in marine sediments at each sampling location. Sampling locations are indicated by the circled numbers. The height of each bar shows the total concentration burden of micropollutants (ng g^{-1}) at each site for each of the two sampling rounds (distinguished by colour). The number inside each bar indicates the number of detected target analytes.

The sediment concentration ranges for OP, BP-3, BPA, E1, and Cstanol from Whakaraupo Harbour are in the lower ranges of internationally detected concentrations, while concentrations of BP-1 and OMC are comparable or slightly elevated to overseas studies (Table 3.8). The micropollutants mParaben and 4-MBC have not been previously detected in marine sediments. A comparable study on the sediments of Auckland Harbour measured concentrations of OP between 100 – 160 ng g^{-1} d.w. and BPA between 50 – 160 ng g^{-1} d.w., which is significantly higher than was measured in Whakaraupo Harbour [203]. The Auckland study did not detect triclosan in any sampled sediments [203], similarly to the Whakaraupo Harbour study. However this may be due to the high detection limit of 100 ng g^{-1} d.w. determined by the Auckland study [203]. In Auckland the steroid hormones E1 and E2 were detected between 0.64 – 2.8 ng g^{-1} d.w. and 0.47 – 1.2 ng g^{-1} d.w. [203]. These E1 concentrations are comparable to the Whakaraupo sediments. The Auckland study did not analyse for UV filters. With the exception of mParaben, all detected analytes were expected to bind to sediments based on their K_{OW} values. Only mParaben, with a K_{OW} of 1.66 [34], would be expected to be too hydrophilic to partition into sediments.

In April, the analytes OP, BP-3, BP-1, BPA, OMC, and Cstanol were detected in at least six of the 14 Whakaraupo Harbour sampling sites, while mParaben was detected at three sites and E3 detected at one. In October, the frequently detected analytes changed to mParaben, OMC, E1, and Cstanol, with these four analytes detected in at least nine sites. Less commonly detected analytes in October were 4-MBC, BP-3, OP, and BPA, which were detected in four, three, two, and one sites respectively. At the Pigeon Bay reference site no target analytes were detected during the April sampling round, except for the fecal steroid Cstanol. This may however have originated from marine mammals rather than sewage [134]. By October however mParaben, 4-MBC, BP-3, and OMC were detected at Pigeon Bay.

No consistent trend was observed for the distribution of analytes in the marine sediment samples from either the April and October sampling period. In April, mParaben was only detected at two sites, while by October mParaben was distributed around most sites throughout the harbour, including Pigeon Bay. The reverse was true for OP, BP-3, and BPA. OP, BP-3, and BPA, all of which were detected throughout the harbour in April. However by October OP and BP-3 were only detected at two sites, and BPA only at one. In April, the UV filter BP-1 was only detected in the inner harbour area (sites 2 – 7). The other UV filter 4-MBC was predominantly detected in the outer harbour areas (sites 11 – 13), as well as at site 5 (Governors Bay outfall), and Pigeon Bay. These changes between April and October may have been caused by strong winds and ocean currents which can mix and re-suspend the bottom sediments, allowing them to be flushed out of the harbour and be replenished by fresh sediments from eroding hillsides. Sediment re-distribution may have also occurred for OMC,

as it was detected only around the inner harbour in April (sites 1- 7), but in October moved exclusively to the outer harbour (sites 7 – 13 and Pigeon Bay). High sedimentation rates experienced in Whakaraupo Harbour [171] would increase during high precipitation periods such as winter, and may quickly replenish sediments and bury any sewage affected sediments. Lastly, E3 was detected once in April. E1 was not detected in the April samples, but by October was present at all sites except Pigeon Bay.

Despite the continuous release of triclosan and methyl triclosan into the harbour via the sewage effluents (Section 3.3.4) these compounds were never detected in the sediments. Due to its physical and chemical properties triclosan usually associates with suspended particulates and sediments [62, 186, 196, 197]. Previously reported concentrations in river, estuary, and lake sediments are between 0.3 – 1,329 ng g^{-1} [62]. Following partitioning into sediments triclosan can cease to degrade, and may potentially remain stable for many decades [166, 222].

UV filters were the most common group of analytes detected in the sediments (Table 3.8). The occurrence of UV filters in sediments has received much less attention than their occurrence in the aqueous phase [40, 223]. Therefore there is limited literature available on the presence of UV filters in sediments. There is insufficient data available to create a realistic picture of their environmental fate [40]. Based on their K_{OW}'s it is postulated they should predominantly associate to sediments [40], and UV filters have been reported to accumulate in sediments to low ng g^{-1} levels [40]. However mass-balance investigations suggest other mechanisms are involved in their removal from the environment, some of which may be of photochemical origin [40].

The range of OMC concentrations in Whakaraupo Harbour were <0.6 – 11.5 ng g^{-1} d.w., exceeding the maximum concentration of 9 ng g^{-1} d.w. detected in Lebanese coastal sediments [209]. In French coastal lagoon sediments the concentrations of OMC reached 1.6 ng g^{-1} d.w., increasing to 2.5 ng g^{-1} d.w. at a marine outfall [209]. This Mediterranean study detected a range of UV filters in the coastal zones (river outfalls, transitional zones, and upstream of rivers) of the eastern and western Mediterranean (Lebanon and France respectively) [209]. There were statistically significant differences in UV filter concentrations between each of the three physical zones in Lebanon. Concentrations were highest upstream of rivers, and lowest at the coast. However there were no seasonal trend in UV filter concentrations in the coastal sediments, as in Whakaraupo Harbour. UV filter concentrations were lower in France than Lebanon, most likely because of better wastewater treatment facilities [209].

OMC concentrations between August and September in Japanese river sediments were considerably higher still, ranging from 2.0 – 101 ng g^{-1} d.w. [84]. However, the study could not detect any 4-MBC or BP-3, both of which were detected in Whakaraupo Harbour between

1.8 – 4.5 ng g^{-1} d.w. and <0.8 – 1.6 ng g^{-1} d.w. for 4-MBC and BP-3 respectively. A Californian study could not detect any BP-3 at its coastal sampling sites, all of which were located by sewage outfalls [165]. BP-3 and BP-1 were however prevalent in US river sediments, ranging between 0.728 – 4.66 ng g^{-1} d.w. and 0.259 – 0.607 ng g^{-1} d.w. respectively [206]. BP-3 levels were lower in Chinese river sediments, ranging between 0.272 – 0.545 ng g^{-1} d.w. [206].

OP was detected infrequently in the Whakaraupo sediments and seawater. OP is relatively resistant to degradation in the environment [100, 197], and has been shown to strongly associate with sediments [197]. Similarly, BPA tends to associate with sediments more than with water, and can range in concentration from <0.5 – 1,630 ng g^{-1} [126]. Under anaerobic conditions BPA can persist for prolonged periods of time, but bacteria, plankton, and plants have been shown to be able to remove BPA from the aquatic environment [126]. However there is little evidence of anaerobic conditions in Whakaraupo Harbour [175]. BPA was found at elevated concentrations in sediments around the reclamation area, and may have come from the Lyttelton outfall or the adjacent reclamation process.

Marine sediments in the vicinity of WWTP outfalls may be more impacted by micropollutants than other sites. In Whakaraupo Harbour sediments 4-MBC was only detected in October at three sites at the harbour entrance, and at site 5 by the Governors Bay WWTP outfall. The sediment concentrations of BPA were always highest at the Lyttelton WWTP outfall (site 9), which was also one of only two sites in October where BP-3 and OP were detected. Site 7 by the Diamond Harbour WWTP outfall showed no patterns. This may be because the strong currents which flow by this point in the harbour [174], quickly carring away and diluting any micropollutants. Internationally, sediment samples from sewage outfall sites have been observed to be most heavily impacted by micropollutants. In Tokyo Bay, levels of BPA, NP, E1, and E2 were elevated at a WWTP outfall site compared to other sites [168]. In the Californian Bight pharmaceuticals and PCPs, including triclosan and NP, were also elevated at the outfall site compared to a reference site [165]. A study in Hamilton Harbour found sediment concentrations of OP quickly decreased over a distance of a few hundred meters from the sewage discharge [201].

3.3.7 Green Lipped Mussels

The mussel tissue concentrations from each of the two sampling rounds are presented in Table 3.9, along with the range and frequency of detected analytes and a comparison to international literature ranges. Because no standard exists on the reporting of biota concentrations, studies report detected analytes on a dry weight (d.w.), wet weight (w.w.), or lipid weight (l.w.) basis. For ease of comparison the concentrations obtained by this study have been reported using all

three approaches. The complete data are provided in Appendix A Table 8.11 where all analyte spike and surrogate recoveries, as well as dry weight and lipid weight percentages can also be found. As mentioned in Section 3.2.4, due to severe matrix interferences only the surrogates $^{13}C_6$-mParaben, $^{13}C_6$-bParaben and $^{13}C_6$-E2 could be recovered, with acceptable spike recoveries only achieved for mParaben, eParaben, OP, pParaben, BP-3, E2, EE2, and E3.

Table 3.9: Concentrations (ng g^{-1}) of detected analytes by dry weight (d.w.), wet weight (w.w.), and lipid weight (l.w.) in New Zealand green lipped mussels collected in April 2012 and January 2013, with comparisons to data from international aquatic biota [a].

Analyte		April 2012	January 2013	Literature Range	Reference
mParaben	d.w.	5.0 – 21.3 (5/5)	4.6 – 14.0 (4/4)	0.86 – 2.3 μg g^{-1} w.w.	[113]
	w.w.	1.1 – 4.1	0.9 – 2.5		
	l.w.	237.4 – 2218.9	368.4 – 2399.8		
OP	d.w.	3.8 – 8.9 (3/5)	2.7 – 6.5 (4/4)	2.7 – 18.6 ng g^{-1} w.w.	[224]
	w.w.	0.9 – 1.9	0.5 – 1.2	6.7 – 44.9 ng g^{-1} w.w	[131]
	l.w.	281.3 – 926.9	264.4 – 1116.0	3190 – 4920 ng g^{-1} l.w.	[201]
BP-3	d.w.	ND	19.1 (1/4)	11.2 – 24.3 ng g^{-1} d.w.	[225]
	w.w.	ND	3.7	22 – 298 ng g^{-1} l.w.	[103]
	l.w.	ND	2379.5	<50 – 151 ng g^{-1} l.w.	[83]
				66 – 123 ng g^{-1} l.w.	[56]

ND = not detected

[a] biota reference values include biota samples other than mussels (clams, squid, fish, etc)

The micropollutants detected in the green lipped mussel composites were mParaben, OP, and BP-3. mParaben was detected in all mussel samples, ranging between 5.0 – 21.3 ng g^{-1} d.w. in April, and 4.6 – 14.0 ng g^{-1} d.w. in January. There were no statistical differences in the concentrations of mParaben between April and January (paired t-test, $p = 0.1652$), most likely due to the limited sample size. Concentrations of mParaben were generally lower in mussels from the two reference sites Port Levy and Pigeon Bay. In April OP was only detected in mussels from Battery Point, Rapaki, and Sandy Bay (8.9, 8.8, and 3.8 ng g^{-1} d.w. respectively). In January OP was detected in all mussel composites, including Port Levy and Pigeon Bay (2.7 and 4.0 ng g^{-1} d.w.). BP-3 was detected only once in Port Levy mussels (19.1 ng g^{-1} d.w.) in January.

There is limited comparative data for the bioaccumulation of micropollutants in mollusks, which have to date been shown to accumulate alkylphenols [131, 201], UV filters [83, 226], and BPA [131]. Data on the bioaccumulation of micropollutants in fish is more readily available, and studies have shown the bioaccumulation of alkyphenols [100, 131], UV filters [56, 83, 103], triclosan [117, 118], BPA [130, 131, 212], and paraben preservatives [113, 114]. Mussels and fish have distinctly different modes of feeding, and uptake mechanisms for micropollutants and therefore tissue concentrations are likely to be different. Due to the filter-feeding nature of mussels they filter many liters of water each day, and therefore provide a useful biological integrator for contaminants that are present in water at very low concentrations [227].

Detected concentrations of OP in the Whakaraupo Harbour mussels tissue were lower than has been reported internationally. In Singapore, OP has been detected at concentrations between 6.7 – 44.9 ng g^{-1} w.w. in seafood such as clams, squid, and fish [131]. In the US, transplantation studies have shown that bioaccumulation of OP and NP in mussels decreases with decreasing distance from WWTP discharges in the Detroit River [201]. Environmental disturbance was therefore concluded to be localized to the point of discharge [201]. Mussels collected in January from the Port Levy and Pigeon Bay reference sites however contained OP, suggesting that environmental disturbance may occur over a larger area than previously thought. In Singapore, the wide distribution of alkylphenols in biota was attributed to the ubiquitous boat traffic [131], and shipping activity may be a possible source of OP in and around Whakaraupo Harbour.

BP-3 was detected in only one mussel sample. Until recently no data on marine mussels were available. OMC has now been detected in marine mussels from the Atlantic and Mediterranean, with a range of 3 – 256 ng g^{-1} d.w. [226]. OMC was detected in mussels sampled throughout the year, with an increase observed in summer, and concentrations highest at sites with high recreational use [226]. Furthermore, mussels sourced from enclosed marine areas had elevated concentrations compared to mussels sourced from less sheltered areas [226].

There is limited data on the bioaccumulation of paraben preservatives in aquatic biota, in particular mollusks. Laboratory fish exposure studies have shown mParaben and pParaben can accumulate in fish [113, 114]. The bioaccumulation of paraben preservatives may not have been previously assessed because the octanol/water coefficients (K_{OW}) are relatively low, ranging from 1.66 for mParaben to 3.24 for bParaben [34]. Accumulation processes other than lipid partitioning can possibly explain the observed bioaccumulation of mParaben. Partitioning into non-water and non-lipid cellular components of an organism may influence the uptake of certain chemicals via protein or active transport processers rather than through simple passive diffusion [228].

The potential for specific chemicals to bioaccumulate can be represented using bioconcentration factors (BCFs) or bioaccumulation factors (BAFs). BCFs are determined from laboratory studies and do not take into account protein or active transport processes or dietary intake [228, 229]. BAF factors are determined using field studies, and take into account all possible biological interactions, including biomagnifications effects (i.e trophic transfer) [229]. The data from this Lyttelton study cannot calculate BCFs because the data was obtained using field samples. Nor can it be used to calculate BAFs as the dietary

exposure of the mussels was not determined. A simple concentration factor was calculated instead using equation (1),

$$CF = \frac{C_{biota}}{C_{aq}} \qquad (1)$$

where C_{biota} = wet weight concentration of analyte in biota, C_{aq} = concentration of analyte in the aqueous phase.

Using the average mParaben and OP water concentration of 0.5 ng L^{-1} in the Whakaraupo Harbour seawater (based on measured concentrations in Section 3.3.5), and using the minimum and maximum detected tissue concentrations, calculated CFs range between 2,200 – 8,400 for mParaben and between 1,800 – 3,800 for OP. Using an average BP-3 water concentration of 3 ng L^{-1} the w.w. based CF for BP-3 is 6367 for the single detection of BP-3. BCFs of OP in fish have been estimated to range between 267 – 471 [100], which is lower than the concentration factor of 1,800 – 3,800 approximated in this study. However these differences may arise from the filter feeding nature of the mussels compared to the feeding behaviour of fish. The bioaccumulation of organochlorines in a marine food web has shown higher concentrations of organochlorines in fish compared to mussels, possibly due to the difference in trophic level [230]. No BCF or BAF values for mParaben or BP-3 could be found in the international literature.

It is probable that with improved extraction and clean-up steps adequate recoveries of the remaining target analytes could be achieved. Because of the presence of micropollutants such as 4-MBC, OMC, and BPA in the harbour waters and sediments it is likely they are also present in biota. Triclosan and/or methyl triclosan may also be present in the biota despite their absence in the sediments, due of their lipophilic nature. However, mussels collected from the well flushed San Francisco Bay showed only a small proportion of analytes (pharmaceuticals, PCPs, and alkylphenols) bioaccumulated in the mussel tissues [228]. Photochemical degradation was speculated to be a contributing factor to this [228]. Further studies are therefore required to ascertain the presence of 4-MBC, OMC, BPA, triclosan, and methyl triclosan in Whakaraupo Harbour mussels.

Internationally, UV filters such as BP-3, 4-MBC, and OMC are some of the most commonly detected UV filters in the aquatic environment, and often occur together in the same organism [56, 103, 159]. OMC is of particular concern due to its potential for biomagnifications and its widespread detection in aquatic organisms in,cluding crustaceans, mollusks, and fish [83]. Calculated bioconcentration factors (BCFs) for OMC were 167 – 1,500 [83].

Triclosan has also been shown to bioaccumulate in a number of trophic species, including algae [117], snails [117], fish [117, 118], and dolphins [73]. Triclosan can be biotransformed to the more lipophilic mTriclosan during wastewater treatment [62, 99]. This compound is of greater environmental concern due to its higher potential to bioaccumulate [62]. Bioaccumulation of mTriclosan was observed in algae [117], snails [117], and fish [63, 99, 117, 119]. Bioaccumulation factors (BAFs) for triclosan and methyl triclosan have been estimated at 1,600 and 1,100 respectively [231].

BPA has been shown to bioaccumulate in fish exposed to wastewater effluent [130], and has been detected in freshwater fish [212] and marine fish [131, 212]. BPA was also detected in fish in locations with no detectable levels of BPA in the water phase [212]. This was likely due to the migratory nature of the fish [212], and highlights the importance of BPA being able to be introduced into previously unimpacted food chains [212].

3.4 Potential for Endocrine Disruption and Toxic Effects

The presence of micropollutants in Whakaraupo Harbour seawater, marine sediments, and mussels may pose a risk to the marine organisms living in and around the harbour. The wide distribution of micropollutants in marine sediments shows sediment dwelling organisms are exposed to micropollutants. The presence of micropollutants in green lipped mussels supports the hypothesis that a similar range of micropollutants will most likely be present in other filter feeding and sediment dwelling organisms and may serve as a point of entry into the marine food chain. None of the commonly target analytes were detected in the seawaters at concentrations above 10 ng L^{-1}. These maximum aqueous concentrations of detected micropollutatns were orders of magnitude lower than those reported to induce biological effects, including growth endpoints, endocrine disruption and acute toxicity [1, 105, 109, 112, 123, 124, 126, 129, 232]. However, due to their strong biological activity only small amounts of steroid hormones (low ng L^{-1}) are required in the aquatic environment to cause endocrine disruption in biota [66, 132]. Concentrations of EE2 as low as 1 ng L^{-1} have been shown to induce egg production in fish [233], concentrations of 5 – 6 ng L^{-1} EE2 have lead to the collapse of a fathead minnow population in a lake [234], and life-long exposure of 5 ng L^{-1} of EE2 has led to reproductive failure in zebrafish [235]. Only E1 and E3 were detected in Whakaraupo Harbour, and are less estrogenic than the potent EE2 [29]. The regular presence of E1 in the aqueous phase may however still be a cause of concern due to the potential for chronic exposure effects.

Maximum concentrations of micropollutants detected in the Whakaraupo sediments were 1.7 ng g^{-1} d.w. for mParaben, 2.5 ng g^{-1} d.w. for OP, 4.3 ng g^{-1} d.w. for 4-MBC, 1.6 ng g^{-1} d.w. for BP-3, 1.3 ng g^{-1} d.w. for BP-1, 9.9 ng g^{-1} d.w. for BPA, 11.5 ng g^{-1} d.w. for OMC, and <2.0

ng g^{-1} d.w. for E1. Micropollutants in sediments are thought to contribute to the estrogenicty of marine sediments [82, 168, 207, 236]. Sediment exposure experiments on the freshwater snail *Potamopyrgus antipodarum* has been shown to exhibit developmental problems at even the lowest exposure levels of BPA and OP used in the study [236]. Lowest observed effect concentrations were at 1 ng g -1 for both BPA and OP [236]. The sediment concentrations of OP and BPA measured in the Whakaraupo sediments are higher than those required to adversely affect *Potamopyrgus antipodarum* [236]. Chinese river sediments containing OP, NP, BPA, E1, and triclosan were shown to exhibit an estrogen equivalency (EEQ) of up to 6.04 ng g^{-1} E2 [32]. The highest estrogenic risk areas were identified to occur along metropolitan river sections and by the lower reaches of the river system [32]. Sediments from Tokyo Bay also containing NP, BPA, E1, and E2 had sediment EEQ values ranging between 2.07 – 12.1 ng g^{-1} E2 [168]. Further studies are required to investigate the potential endocrine disrupting and toxicity effects on marine invertebrates. However all target analytes detected in Whakaraupo sediments have been shown to exhibit some biological activity.

3.5 Conclusions

This study has shown that the effluents of the Lyttelton, Governors Bay, and Diamond Harbour WWTPs are a source of micropollutants into Whakaraupo Harbour. Sewage effluents were found to contain mParaben, eParaben, pParaben, bParaben, OP, 4-MBC, BP-3, BP-1, triclosan, methyl triclosan, BPA, E1, E2, EE2, E3, and Cstanol. However only OP, 4-MBC, BP-3, BP-1, triclosan, methyl triclosan, BPA, and E1 were commonly detected in the effluents of all three WWTPs. The concentration patterns of triclosan, methyl triclosan, E1, and Cstanol did not vary between WWTPs. However, despite the fact each WWTP is based on the same treatment design and located in the same geological area, distinct differences were observed in each WWTP for the other frequently detected analytes. In terms of analyte concentration trends the Lyttelton WWTP was found to be most consistent, while the Governors Bay WWTP was the most variable. There is evidence that key events such as heavy rain events and chemical spills had an impact on the treatment efficiencies of all three WWTPs. The concentrations of some analytes exhibited signs of seasonality, in particular in Lyttelton. Seasonal trends in Lyttelton (for OP, 4-MBC, triclosan, methyl triclosan, BP-1, BPA, and Cstanol) and Governors Bay (for triclosan, methyl triclosan, and BPA) showed an increased concentration in colder months over warmer months. In Diamond Harbour the same pattern was observed for triclosan and BPA, while the opposite was true for 4-MBC and BP-3.

Monitoring of the receiving seawater confirmed the presence of micropollutants at concentrations close to the method detection limit. Regularly detected analytes were mParaben, 4-MBC, BP-3, BPA, OMC, and E1. Of these only 4-MBC, BP-3, BPA, and E1

were also regularly detected in the sewage effluents discharged into Whakaraupo Harbour. Despite the release of OP, triclosan, methyl triclosan, BP-1, and Cstanol from effluent only OP and BP-1 were only occasionally detected in seawater. Upon release into the harbour environment these infrequently detected micropolluants may either photo-degrade or associate with suspended materials, where they can either settle into harbour sediments or be flushed out of the harbour via the currents. The occurrence of mParaben and OMC in the seawater but not the sewage effluent suggests as yet unknown sources or release mechanisms into the environment. A number of analytes were also regularly detected the seawaters from the Pigeon Bay reference site, highlighting the difficulties of locating a suitable reference site for the analysis of organic micropollutants.

Harbour sediments were found to be a sink for micropollutants. Sediments were found to accumulate mParaben, OP, 4-MBC, BP-3, BP-1, BPA, OMC, E1, and Cstanol. However the concentration of sediments differed greatly between April and October. Strong winds and currents are likely to cause strong mixing and re-suspension of the sediments, allowing them to be flushed out of the harbour and be replenished by fresh sediments from eroding hillsides.

mParaben, OP, and BP-3 were found to bioaccumulate in green lipped mussles. Due to poor extraction performance the majority of target analyets could not be adequately recovered. With an improved methodology other analytes including 4-MBC, BPA, and OMC are likely to also be detected in the mussel tissues. BP-3 was only detected in mussel tissues sampled from Port Levy in January 2013. mParaben and OP were detected in mussel tissues from all other sites, including the reference sites at Port Levy and Pigeon Bay. Mussels from within the harbour at Battery Point, Rapaki, and Sandy Bay contained slightly higher levels of micropollutants than those sampled from the reference sites.

CHAPTER FOUR

SOURCES AND DISTRIBUTION OF MICROPOLLUTANTS IN EREBUS BAY, ANTARCTICA

4 Sources and Distribution of Micropollutants in Erebus Bay, Antarctica

4.1 Introduction

Antarctica is acknowledged as one of the last remaining places on Earth untouched by humans. However, the majority of scientific research stations are located adjacent to the coast, where their industrial and household sewage is released into the coastal seawater [237, 238]. Under Annex III of the Protocol on Environmental Protection to the Antarctic Treaty (Article 5), liquid sewage needs to only be macerated before being discharged into the aquatic environment [239]. As a result, the wastewaters from 37% of permanent research stations and 69% of summer stations lack any kind of treatment. Furthermore, the Antarctic research stations with WWTPs have reported being unable to cope with the high influx of wastewater during the summer season [240]. Some stations regularly encounter operational problems and malfunctions during summer, or throughout the year, from fluctuating water inflows, frozen pipes, or reduced microbial activity within the plant due to low temperatures in winter [240]. In addition, some research field parties stationed for long periods along the coast or on the sea ice to conduct their field work are allowed to dispose of raw human waste and grey water directly into the ocean via tidal cracks in the sea ice [241], a practice referred to as 'tide-cracking'. Ships are also allowed to release food waste and sewage into the ocean, but at a distance of at least 12 nautical miles from the coast or ice shelf [242]. A large amount and a wide variety of micropollutants are therefore likely to enter the Antarctic aquatic environment.

The majority of studies on micropollutants have been conducted in temperate climates, and understanding the factors that determine their environmental fate and behaviour is currently an area of intense research. In contrast, there is limited data on the fate and behaviour of micropollutants in the polar environments. Fieldwork in Antarctica is particularly challenging, with high costs and logistical challenges limiting the number of environmental studies on aquatic pollution. To date, studies of organic contaminants in the Antarctic environment have focused on more hydrophobic and persistent organic pollutants in both seawater and wildlife [139, 143, 145]. Micropollutants such as steroid hormones and micropollutants from PCPs have so far not been investigated as environmental pollutants in the Antarctic.

PCPs, particularly sunscreens and moisturizers are high use products in Antarctica due to the dry atmosphere and high UV light conditions. In addition large volumes of soaps, shampoos, detergents, and disinfection products are used to maintain an adequate level of hygiene to minimise the risk of disease. Micropollutants most commonly associated with these PCPs are

UV filters [1], paraben preservatives [1], triclosan [62], alkylphenol ethoxylates [120, 121], and BPA [22]. As a consequence a large amount and wide variety of micropollutants derived from PCPs likely enter the WWTPs of Antarctic research stations, which may not adequately be removed during treatment, and end up being released into the Antarctic aquatic environment. The prevailing climatic conditions, in particular the cold temperatures, extended periods of darkness, and the presence of sea ice covering coastal sea waters for a large part of the year, may reduce the degradation and therefore extend the persistence of micropollutants in Antarctic coastal environments.

Two field studies were conducted to investigate the presence of micropollutants in Antarctica. A small preliminary study was conducted in October during the summer research season of 2009/2010 to determine if micropollutants were present in the sewage effluents of Scott Base and McMurdo Station and the receiving coastal environment, and to collect marine biota for subsequent analysis. A larger study was conducted over November/December during the summer research season of 2012/2013 to investigate the distribution of PCPs over a wider area around the research stations.

The specific objectives of these studies were to:

- Identify and quantify micropollutants within the WWTP effluents of Scott Base and McMurdo Station on Ross Island,
- determine the concentration and distribution of micropollutants in the seawaters of Erebus Bay which receive these WWTP discharges,
- determine if micropollutants accumulate in aquatic biota living in Erebus Bay,
- provide a preliminary assessment of the potential risk these micropollutants may pose to Antarctica's unique marine ecosystem.

This chapter presents the findings and outcomes of these investigations.

4.2 Methods

All details regarding the extraction of the sewage effluent and seawater samples, laboratory QA/QC, the preparation and extraction of the biota samples, and the analysis of the samples by GC-MS are provided in Chapter 2. This section provides information on the study area, the sewage treatment plants of Scott Base and McMurdo Station, and the sampling strategy implemented during the 2009/2010 and 2012/2013 research seasons.

4.2.1 Study Area

Ross Island is a volcanic island situated in the McMurdo Sound region of the Ross Sea in Antarctica (Figure 4.1). To the south the island is bordered by permanent ice from the Ross Ice Shelf. The remainder of the island is surrounded by annual sea ice which begins to break up and disperse between December and February [243]. The two research stations Scott Base (New Zealand) and McMurdo Station (USA) are located on Hutt Point Peninsula, located in the southwest of Ross Island. The coastal area adjacent to the two research stations is called Erebus Bay, and stretches as far north as Cape Royds. Scott Base and McMurdo Station can house up to 86 and 1,200 personnel respectively over summer [146], with a reduced population of approximately 12 [241] and 250 [244] staff respectively over winter. The population of Scott Base over the 2012/2013 research season is presented in Figure 4.2. The sewage effluent combines both household and industrial sewage. Sewage has been discharged into the adjacent coastal area since the establishment of the bases. Sewage treatment was only introduced in the 1990s.

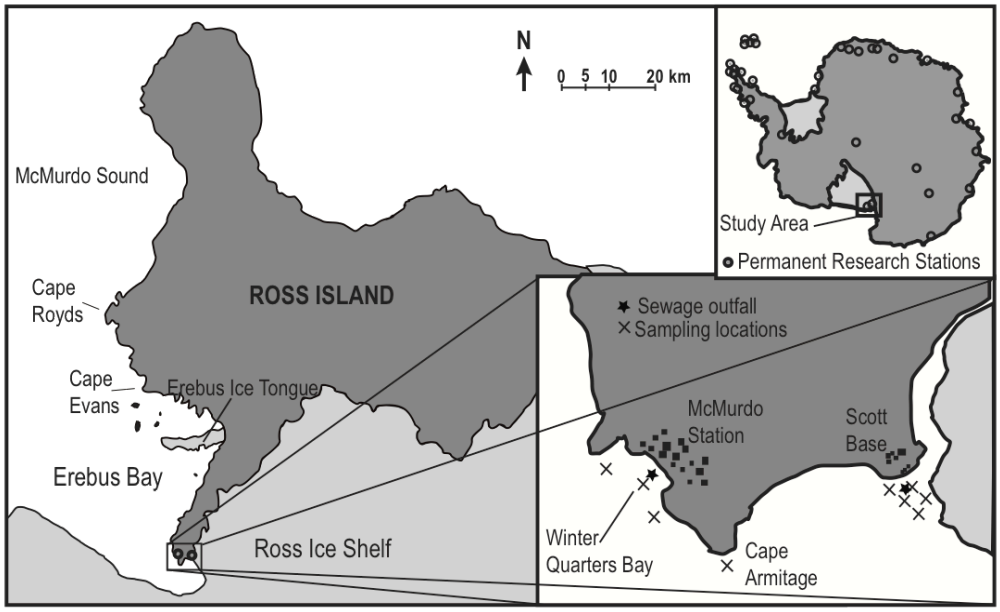


Figure 4.1: Study area and sampling locations of the 2009/2010 research season field trip in Erebus Bay, Antarctica.

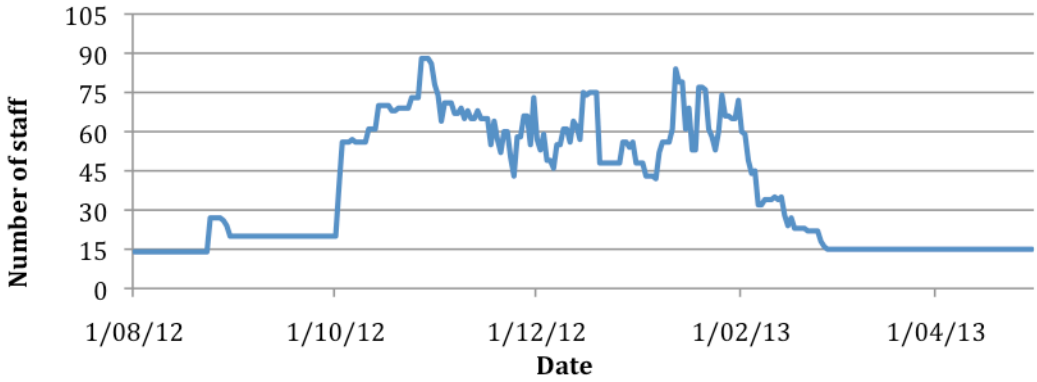


Figure 4.2: Population of Scott Base over the 2012/2013 research season (Antarctica NZ, unpublished data [245]).

4.2.2 Currents

The topography of the region is highly complex, giving rise to complex localized ocean current features, and making their accurate descriptions difficult. This is because ocean currents can vary greatly over short distances along the coast due to the effects of tides, bottom topography, and coastline geometry [246]. The overall currents flow from the north of the McMurdo Sound in a south-easterly direction along Ross Island into Erebus Bay, before diving underneath the Ross Ice Shelf [247]. As the water descents below the ice shelf the flow turns west, before flowing north along the western side of the McMurdo Sound [247]. The current splits in two at Cape Royds, with some of the water being deflected westwards. The Erebus Ice Tongue and the cold water flowing northwards from underneath the ice shelf causes some re-circulation of the water in Erebus Bay [247, 248], and ocean gyres have been observed near the research stations and off Cape Royds [244, 247]. The speed of the currents depend on the tide and location, and speeds of 1 – 2 cm s^{-1} [244], 10 – 20 cm s^{-1} [249], 5 – 60 cm s^{-1} [250], and < 1 cm s^{-1} [251] have been reported. The speeds were reported to remain constant with depth [250, 251].

4.2.3 Sewage Treatment and Disposal

4.2.3.1 Antarctic Sewage Treatment Plant Designs

The sewage treatment system at Scott Base was commissioned in October 2002, and was designed to treat up to 120 person equivalents of wastewater per day. Scott Base produces up to 17,000 litres of wastewater per day during the summer season, combining human waste and grey water for treatment [252]. The daily effluent flows over the 2012/2013 research season are presented in Figure 4.3. Before the start of the season the effluent outflows were as low as ~1,300 L per day, increasing to up to ~8,500 L per day over the summer season. The wastewater is treated by passage through a series of aerated fixed biofilm beds. The plumbing system across Scott Base is divided into several sections, with each section containing its own

wastewater storage tank which services a particular part of Scott Base (i.e. kitchen, living quarters, hangar, etc). Once full the contents of each storage tank are pumped into the WWTP, which, depending on use, are emptied between once every few days (hangar) to several times per day (living quarters), giving rise to an irregular water inflow into the WWTP. The plant uses biological treatment (aerated fixed thin-film beds). Operating temperatures range from approximately 9°C in winter to approximately 26°C in summer due to increased inputs of hot water from showers and laundry. The WWTP temperatures over the 2012/2013 season are presented in Figure 4.4. Before the start of the research season the minimum temperature was 13°C, which steadily increased over the summer season to a maximum of 25°C by the end of the season in February. Solids are removed from treated sewage effluent via centrifuge filtration prior to discharge, and are shipped to New Zealand for disposal. The plant has an operating tolerance of up to 28% seawater, and was designed to cope with rapidly changing influent volumes [253].

The Scott Base effluent undergoes disinfection before discharge into the ocean. Up until the 2009/2010 season disinfection was achieved by UV irradiation. After sampling for the preliminary study was completed the UV irradiation unit was replaced with an ozone disinfection unit designed to provide an ozone contact time between 10 – 15 minutes. Due to difficulties experienced in obtaining replacement parts the Scott Base WWTP ozonation plant was out of operation for the majority of the 2012/2013 research season. The maintenance of sewer systems and WWTP facilities in Antarctica are resource and time intensive activities, and this is the main reason why many Antarctic research stations do not operate a WWTP. Maintenance of the Scott Base sewage system includes desludging the treatment tanks, emptying grease traps, and cleaning filters.

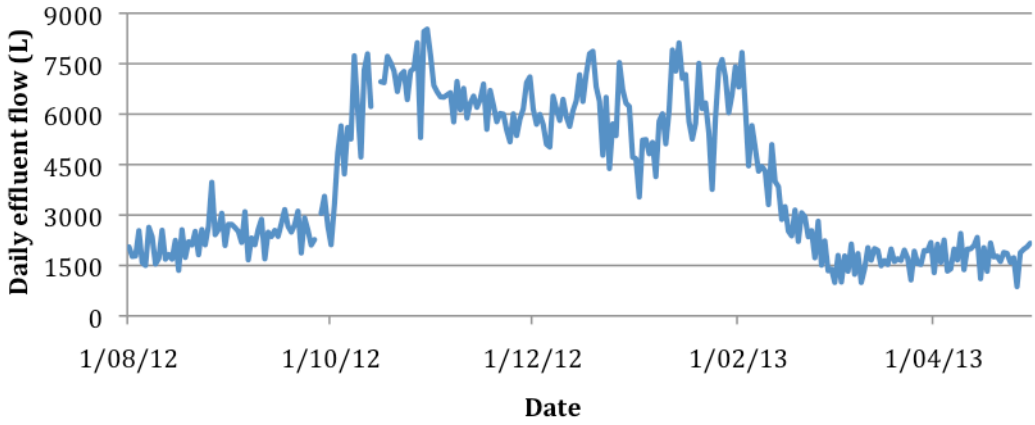


Figure 4.3: Daily effluent outflow (L) of the Scott Base WWTP over the 2012/2013 research season (Antarctica NZ, unpublished data [245]).

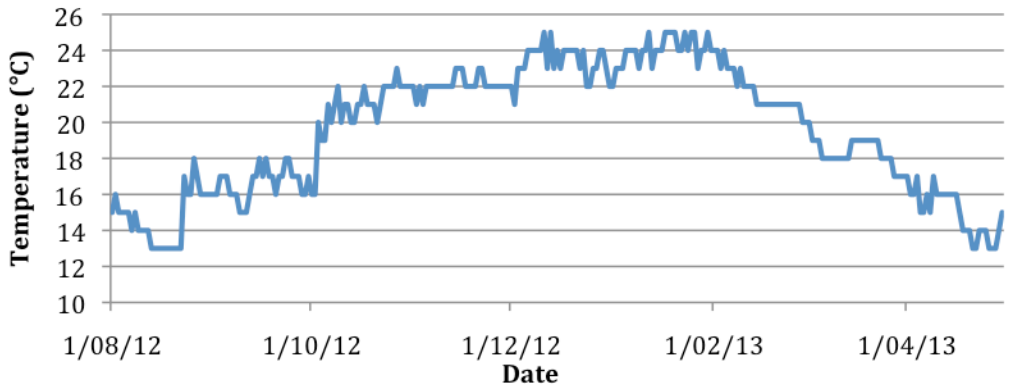


Figure 4.4: Temperature (°C) of the Scott Base WWTP over the 2012/2013 research season (Antarctica NZ, unpublished data [245]).

The McMurdo Station WWTP comprises of an extended aeration system using aerobic digestion at room temperature, followed by UV irradiation for disinfection of sewage effluents prior to discharge into the adjacent Winter Quarters Bay [254]. The system was designed to cope with a summer population of 1,200 people and a daily peak discharge of up to 416,000 litres during summer [254]. Construction of the plant was completed in 2002, and began operating the following year. Solids are removed from the effluent prior to discharge, compacted, and shipped back to the United States for final disposal [254]. Prior to the construction of this WWTP all waste was macerated and mixed with brine from the desalination plant before being released directly into the seawater surface [244, 254].

The locations of the WWTP discharge sites of Scott Base and McMurdo Station are shown in Figure 4.1.

4.2.3.2 Tide-cracking

The disposal of raw human waste and grey water from field research parties via tidal cracks in the sea ice is a second waste disposal method. This practice is referred to as 'tide-cracking', and is permitted under special circumstances [241]. Field parties which are stationed for long periods (up to several months) on or near the sea ice are permitted to dispose of their wastes in this way because of the impracticality of transporting the waste back to base for treatment [241]. The practice is monitored and avoided whenever possible, but both the US and New Zealand Antarctic programs have reported tide-cracking several thousand litres of human waste and grey water in a single season at a number of sites throughout the McMurdo Sound and Erebus Bay [241, 255]. The waste released in this manner includes wastewater generated by the airport and ice runway operated by the US Antarctic program. This demonstrates that chemicals in human waste may become more widely distributed than considered possible from fixed point sewage outfalls alone. Since this waste is untreated and undiluted (waste at

Scot Base would be diluted from toilet and shower water) the net quantity of micropollutants it contains may be equivalent to that of a much larger volume of treated sewage effluent. It is also likely to contain micropollutants that would otherwise have been removed during wastewater treatment.

4.2.4 Sample Collection

4.2.4.1 2009/2010 Research Season

During the 2009/2010 research season, seawater samples were obtained from four locations; the coast off Scott Base, Winter Quarters Bay, Cape Armitage located in between the two research stations, and a reference site at Cape Evans (Figure 4.1). Sewage effluent samples were obtained from McMurdo and Scott Base on one occasion. Sampling was carried out at the beginning of the summer research season, between the 23rd – 31st of October 2009. Samples of WWTP effluent (~4 L) were obtained from the McMurdo Base WWTP plant as a 24-hour composite sample using an automated sampler. Effluent from the Scott Base WWTP (~2 L) could only be obtained as a grab sample. Samples of WWTP effluent were collected into 4 L pre-washed amber glass Winchesters, capped firmly, and transported to the laboratory where they were immediately acidified to pH 2 using sulphuric acid.

Seawater samples were collected through bore holes in the sea ice drilled using either a Kovac or Jiffy drill. A custom made glass sampler was lowered by hand into the surface water that rose to the surface of the borehole. In this manner samples of 4 L of coastal seawater were obtained at Winter Quarters Bay, Cape Armitage, and 10 L from the Cape Evans sampling sites. Due to equipment breakages the seawater samples off the coast off Scott Base had to be collected from the borehole by hand with a glass beaker. The coastal seawater obtained was collected into 4 L pre-washed amber glass Winchesters, capped firmly and transferred in padded polystyrene boxes for transport to the laboratory where they were immediately acidified to pH 2 using sulphuric acid.

Clams (*Laternula elliptica*) were collected from Winter Quarters Bay by the McMurdo SCUBA team. Sea urchins (*Sterichinus neumayeri*) were collected from Cape Armitage using a remote controlled mini-submarine fitted with a fine-mesh net at the front (Figure 4.5). Fish (*Trematomus bernachii*) were collected from Cape Evans by ice fishing (University of Canterbury Animal Ethics Approval Reference 2009/20R).

Figure 4.5: Remote controlled mini-submarine being fitted with a fine-mesh net used to scoop bottom dwelling marine organisms e.g. urchins and starfish.

4.2.4.2 2012/2013 Research Season

During the 2012/2013 research season, seawater samples were obtained from 24 locations across Erebus Bay, stretching between the sea ice/ice shelf boundary in the south and as far north as Cape Evans (Figure 4.8). Samples were obtained on three separate occasions between the 23rd of November and the 7th of December. Five sites could only be sampled during the third sampling round (Site 15, 16, 18, 19, and 20) as the ice runway used by the US Antarctic Program was still in operation at these locations. The specific details for each site including sampling dates, GPS coordinates, and sea ice and snow cover depths are presented in Table 4.1. The sampling locations are shown in Figure 4.8, Section 4.3.4.3. Seawater samples were collected through bore holes in the sea ice. The first meter of sea ice was drilled using a motor powered Jiffy drill. The hole was subsequently flooded by drilling the remaining sea ice using a hand powered Kovac drill to reduce potential sources of contamination from the Jiffy drill. All Jiffy and Kovac drilling flights were solvent cleaned before use to remove any adhering sunscreen or moisturiser material from previous operators. Once flooded the seawater was sampled by immersion of 4 L pre-washed amber glass Winchesters, capped firmly, and transported to the laboratory. Any old labels were removed from the bottles, and the inside and outside of the bottles thoroughly cleaned with MeOH and ACN prior to use. The bottles were only handled while wearing gloves, and were stored in cardboard boxes during transport to and from the field. Sea ice and snow cover depths were measured after sampling and recorded in Table 4.1. Upon return to the laboratory the samples were immediately acidified to pH 2 using sulphuric acid. During the second sampling round sea ice chips created from the Jiffy drilling process were collected from five locations by scooping the fine ice chips directly into a Winchester bottle. Only ice from the top meter of the sea ice was collected, as the bottom half of the sea ice was becoming saturated with seawater due to summer melting of the ice. The ice was allowed to thaw, and the resulting seawater was filtered, extracted, and analysed in the same manner as the other seawater samples.

Table 4.1: Sampling dates and physical parameters of the 2012/2013 season sampling locations.

Site	GPS Coordinates	Round 1[a]		Round 2[b]		Round 3[c]	
		Ice thickness	Snow cover	Ice thickness	Snow cover	Ice thickness	Snow cover
1	S 77° 37.825' E 166° 21.094'	160 cm	0 cm	158 cm	0 cm	–	–
2	S 77° 38.677' E 166° 23.510'	170 cm	0.5 cm	167 cm	0 cm	–	–
3	S 77° 39.962' E 166° 32.134'	203 cm	0.5 cm	202 cm	0 cm	–	–
4	S 77° 42.358' E 166° 22.180'	191 cm	0 cm	173 cm	0 cm	–	–
5	S 77° 41.634' E 166° 28.626'	193 cm	10 – 15 cm	197 cm	2 cm	–	–
6	S 77° 44.900' E 166° 15.726'	187 cm	10 cm	187 cm	4 cm	–	–
7	S 77° 44.850' E 166° 23.070'	191 cm	5 cm	190 cm	4 cm	–	–
8	S 77° 44.663' E 166° 31.354'	179 cm	0 – 15 cm	180 cm	2 cm	–	–
9	S 77° 47.934' E 166° 18.987'	189 cm	4 cm	202 cm	5 cm	–	–
10	S 77° 47.676' E 166° 27.717'	190 cm	5 cm	189 cm	2 cm	–	–
11	S 77° 47.268' E 166° 38.625'	190 cm	1 – 2 cm	174 cm	3 cm	–	–
12	S 77° 50.913' E 166° 27.879'	191 cm	20 cm	199 cm	10 cm	–	–
13	S 77° 50.904' E 166° 32.272'	201 cm	25 cm	194 cm	25 cm	–	–
14	S 77° 50.967' E 166° 37.240'	188 cm	0 cm	184 cm	0 cm	–	–
15*	S 77° 53.347' E 166° 33.726'	–	–	–	–	200 cm	5 – 10 cm
16*	S 77° 52.557' E 166° 37.164'	–	–	–	–	194 cm	7 – 15 cm
17	S 77° 51.721' E 166° 41.175'	192 cm	30 cm	197 cm	25 cm	197 cm	25 cm
18*	S 77° 53.875' E 166° 37.166'	–	–	–	–	225 cm	25 – 30 cm
19*	S 77° 53.861' E 166° 41.513'	–	–	–	–	214 cm	20 cm
20*	S 77° 53.136' E 166° 41.576'	–	–	–	–	227 cm	0 cm
21	S 77° 52.034' E 166° 49.466'	216 cm	55 cm	228 cm	50 cm	220 cm	45 cm
22	S 77° 51.938' E 166° 46.623'	205 cm	50 cm	200 cm	60 cm	204 cm	55 cm
23	S 77° 51.528' E 166° 43.894'	217 cm	40 cm	229 cm	50 cm	225 cm	30 cm
24	S 77° 51.255' E 166° 47.728'	195 cm	56 cm	199 cm	55 cm	200 cm	56 cm

[a] Sites 1 – 5 + 7 sampled 23rd Nov, Sites 6 + 8 – 19 sampled 24th Nov.

[b] Sites 1 – 8 + 10 sampled 30 Nov, Sites 9 + 11 – 19 sampled 1st Dec.

[c] Sites 15 – 24 sampled 7th Dec.

* Unable to sample during rounds 1 & 2 as the ice runway was still at these locations.

The treated sewage effluent from the Scott Base WWTP was sampled monthly between August 2012 and February 2013 to gain an insight into how micropollutant concentrations fluctuated over the course of one summer research season. Triplicate 1 L effluent samples (1 L duplicates plus a 1 L sample used for spike recoveries) were collected by the base science technician into 1 L amber glass bottles and immediately acidified to pH 2 using concentrated sulphuric acid. The samples were stored on ice until, and during, the flight to Christchurch. Sampling was timed to take place as close as possible to the departure of the plane. However due to regular flight cancelations caused by poor weather or poor ice runway conditions, the sampling intervals were not as regular as initially planned. The glass bottles were wrapped in bubble wrap, double bagged, and transported in padded polystyrene boxes. The samples were collected from the airport in the morning following the sampling of the WWTP, and transported to the laboratory where they were immediately filtered and extracted. All samples were extracted within 72 hours of sampling of the WWTP. In addition to monthly sampling the Scott Base WWTP effluent was also sampled daily over the course of one week (9:30 AM, 9th – 15th Dec 2013) during the 2012/2013 field sampling trip to gain an insight into the short-term fluctuations in micropollutant concentrations. The McMurdo WWTP sewage effluents were not sampled during the 2012/2013 research season because permission from the US Antarctic Program to access their WWTP could not be obtained.

4.2.5 QA/QC

All QA/QC protocol procedures are outlined in Chapter 2.

4.3 Results and Discussion

4.3.1 Data Analysis

All data were stored and edited for statistical analysis in Microsoft Excel (2008 for Mac, Version 12.1.0). All statistical analyses were performed in R (Version 2.14.1 for Mac). Both Excel and R were used to prepare graphics. Statistical analyses of the sewage effluent data were only applied to analytes which were detected in all samples (OP, 4-MBC, BP-3, BP-1, triclosan, methyl triclosan, BPA, E1, and Cstanol). To avoid pseudo-replication all duplicate measurements were averaged before being included in the analyses.

For the seawater data statistical analyses were only performed for analytes that were detected in at least 50% of samples (mParaben, 4-MBC, BP-3, BPA, and OMC). Any duplicate samples were averaged before being used in the analyses. For analytes detected below the LOQ a value of half the LOQ was used in the analyses. Differences between sampling rounds were analyzed using a paired student t-test.

4.3.2 QA/QC

4.3.2.1 2009/2010 Research Season

Data for the individual recoveries of the surrogates spiked into the effluent samples, and the statistical summary, are provided in Appendix B Table 9.1. Data for the seawater surrogate recoveries are provided in Appendix B Table 9.2a, with a statistical summary provided in Appendix B Table 9.2b. Surrogate recoveries were quantified against the corresponding comparative standard prepared for each batch of processed samples. The $^{13}C_{12}$-triclosan and $^{13}C_6$-E2 surrogates were not added to samples during the 2009/2010 field trip as they only became available after completion of the field work.

Surrogate recoveries between the effluent duplicates were similar, but differed between Scott Base and McMurdo, possibly due to matrix effects. Overall average recoveries (mean ± 95% confidence interval) were variable at 102.7% ± 36.6%, 114.0% ± 29.4%, 84.9%% ± 72.9%, and 93.0% ± 35.6% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, and $^{13}C_{12}$-BPA respectively. The average surrogate recoveries are in close agreement with those obtained for WWTP effluents in the Whakaraupo Harbour Study (Section 3.3.2). Average surrogate recoveries (mean ± 95% confidence interval) from the 4 L seawater samples (excluding Cape Evans) were 85.6% ± 6.8%, 90.6% ± 5.0%, 58.3% ± 4.9%, and 106.1% ± 4.5% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, and $^{13}C_{12}$-BPA respectively. These recoveries are also in close agreement with those obtained from the seawater samples in the Whakaraupo Harbour study (Chapter 3, Section 3.2.4), with the exception of $^{13}C_{12}$-BPA, which was ~20% higher in the Antarctic seawater samples. The adequate surrogate recovery levels meant the concentrations of detected analytes in the sewage effluents and seawater samples were not corrected against surrogate recovery. However the MQ blank contributions were subtracted from all samples. The MQ blank contributions and the detected analytes in the comparative standards are provided in Appendix B Table 9.3. Despite the use of gloves, blanks contained several PCPs, with contributions of mParaben and BP-3 being particularly high due to the fact that sunscreen products must be worn in Antarctica for health and safety reasons. Previous studies on PCPs have also reported on the presence of PCPs such as parabens, UV filters, and triclosan in their laboratory blanks [53, 55, 56]. In addition, the results from the seawater samples collected off the coast of Scott Base indicated the measurements of mParaben, pParaben, and BP-3 were compromised, most likely due to the different sampling technique which had to be used. These analytes were therefore excluded from the discussion. These results highlight the inherent difficulties of the trace analysis of personal care products.

Analyte and surrogate spike recoveries for the Antarctic biota can be found in Appendix B Table 9.14. As was the case for the New Zealand mussels (Section 3.3.2), severe matrix

interferences prevented the detection and/or quantification of a number of spiked surrogates and spiked analytes from the fish, clams, and the urchin composite. However the chromatograph was considerably cleaner, and more compounds could be identified compared to the New Zealand mussels. The surrogates $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, and $^{13}C_6$-E2, and the analytes mParaben, eParaben, pParaben, bParaben, OP, BP-3, BP-1, E1, E2, EE2, E3, and Cstanol could be adequately recovered. However, the OP spike could not be adequately recovered for the clam tissue. The variability in the recovery of surrogate spikes was considerably lower than that observed for the NZ mussels, with standard deviations of 11.6%, 10.8%, and 12.8% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, and $^{13}C_6$-E2 respectively. Average recoveries (mean ± 95% confidence interval) were 72.0% ± 5.4%, 71.7% ± 5.1%, and 66.6% ± 6.0% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, and $^{13}C_6$-E2 respectively. Detected analytes were not corrected against surrogate recoveries. Lastly, of the 14 urchin samples only 10 contained useful amounts of roe tissue. The majority of the urchin cavity was filled with water, and enough material for only one single composite sample was obtained.

4.3.2.2 2012/2013 Research Season

Data for the individual recoveries of the surrogates spiked into the effluent samples, and a statistical summary, are provided in Appendix B Table 9.6. Analyte spike recoveries of the matrix spike are provided in Appendix B Table 9.7. No surrogate data are available for the seven-day sewage effluent monitoring study conducted in December 2012 because the surrogate solution was exhausted by the time this work was conducted and the replacement surrogate solution did not arrive in time. The natives spike recoveries were however acceptable. Data for the seawater surrogate recoveries and a statistical summary are provided in Appendix B Table 9.10, and analyte spike recoveries are provided in Appendix B Table 9.12. The surrogate spike recoveries for the sea ice samples are provided in Appendix B Table 9.11. All analyte spike and surrogate recoveries were quantified against the corresponding comparative standard prepared for each batch of analysed samples, and analyte recoveries were not corrected for surrogate recoveries.

Compared to the 2009/2010 surrogate spike recoveries the 2012/2013 surrogate spike recoveries of $^{13}C_6$-mParaben were higher, $^{13}C_6$-NP was lower, and $^{13}C_6$-bParaben and $^{13}C_{12}$-BPA were approximately equal. The recovery of the $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, and $^{13}C_{12}$-triclosan surrogates from the 2012/2013 Scott Base WWTP samples were higher than compared to those from the Whakaraupo Harbour WWTP effluents. Average surrogate recoveries of $^{13}C_6$-NP and $^{13}C_6$-E2 were lower for the Scott Base effluents than Whakaraupo, while $^{13}C_{12}$-BPA recoveries were approximately equal. The variability was approximately equal between Scott Base and Whakaraupo Harbour, with standard deviations of the Scott

Base surrogate spikes at 33.9%, 11.3%, 47.4%, 22.0%, 8.6%, and 13.2% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 respectively. Average recoveries of the 2012/2013 Scott Base WWTP effluent surrogate spikes (mean ± 95% confidence interval, n = 12) were 136.4% ± 21.5%, 116.0% ± 7.2%, 69.7% ± 30.1%, 129.0% ± 14.0%, 89.7% ± 5.5%, and 74.9% ± 8.4% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 respectively. Spike recoveries of some analytes (Appendix B Table 9.7) were sometimes above 120% (mParaben, eParaben, OP, pParaben, BP-3, BP-1), most likely because of matrix enhancement effects during instrumental analysis. The 4-MBC spike could not be adequately recovered in some samples due to its already high concentration in the effluents.

For the seawater, surrogate recoveries of $^{13}C_6$-mParaben and $^{13}C_6$-bParaben were higher in 2012/2013 compared to 2009/2010, while for $^{13}C_{12}$-BPA they were lower, and were approximately equal for $^{13}C_6$-NP. Average recoveries (mean ± 95% confidence interval, n = 57) were 109.% ± 4.4%, 78.9% ± 3.4%, 55.3% ± 4.3%, 116.7% ± 3.7%, 81.6% ± 2.7%, and 84.9% ± 4.3% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 respectively. The variability was also lower compared to the 2009/2010 research season, with standard deviations of 16.7%, 12.7%, 16.2%, 14.1%, 10.0%, and 16.4% for $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, $^{13}C_6$-NP, $^{13}C_{12}$-triclosan, $^{13}C_{12}$-BPA, and $^{13}C_6$-E2 respectively. Acceptable analyte spike recoveries (Appendix B Table 9.12) were also achieved. However some recoveries were over 120%, but was thought to come from reduced comparative standard values, the cause of which is currently unknown.

4.3.3 Sewage Effluents

4.3.3.1 2009/2010 Research Season

Seven analytes were detected in the Scott Base WWTP effluent, while only three analyes were detected in the McMurdo WWTP effluent. The concentration range and frequency of detected analytes are presented in Table 4.2 and are comparable to concentrations measured internationally (Table 4.2). Analyte concentrations of the individual WWTPs are provided in Appendix B Table 9.4. The Scott Base WWTP effluent contained 4-MBC, BP-3, BP-1, BPA, E1, OP, and triclosan. The McMurdo WWTP effluent only contained BP-3, BP-1, and BPA. The concentration of BP-3 was lower in the Scott Base WWTP effluent than the McMurdo WWTP effluent (89.7 ng L^{-1} vs. 130.7 ng L^{-1} respectively), and that of BP-1 was higher (170.7 ng L^{-1} vs. 7.3 ng L^{-1} respectively). The concentration of BPA was similar in both effluents (31.9 ng L^{-1} vs. 28.0 ng L^{-1} respectively). Scott Base and McMurdo utilize different treatment processes to treat their wastewater (aerated thin-film beds vs. extended aeration), which was a likely cause of the observed differences. There may also be differences in the

types of personal care products and frequency of their use between the two research stations. Both stations disinfected their effluent with UV irradiation at the time of sampling. No paraben preservatives were detected in the WWTP effluents of Scott Base and McMurdo Station, as was observed in the Whakaraupo Harbour study. Inadequate extraction efficiency of the method can be excluded because of the acceptable surrogate recoveries obtained for the surrogate compounds $^{13}C_6$-mParaben and $^{13}C_6$-bParaben for these sewage effluent samples.

Table 4.2: Concentration range (ng L^{-1}) and comparison to literature values of target analytes in WWTP effluents from the 209/2010 and 2012/2013 Antarctic research season.

Analyte	Season	Frequency	Range	Literature range	Reference
mParaben	09/10	0/2	ND	2.1 – 423	[47-49]
	12/13	2/13	22.7 – 36.4		
eParaben	09/10	0/2	ND	<0.3 – 1,600	[47, 49, 256]
	12/13	0/13	ND		
OP	09/10	1/2	101.1 – 118.0	3.7 – 3,949	[49-51]
	12/13	13/13	7.5 – 7,053.8		
pParaben	09/10	0/2	ND	<0.5 – 95	[47, 49, 184]
	12/13	0/13	ND		
bParaben	09/10	0/2	ND	<0.2 – 83	[46, 47, 50, 51]
	12/13	1/13	9.7 – 11.0		
NP	09/10	0/2	ND	<29 – 3,210	[47, 50, 51]
	12/13	0/13	ND		
4-MBC	09/10	1/2	173.0 – 216.8	42 – 2,300	[56-58]
	12/13	13/13	320.7 – 11,725.9		
BP-3	09/10	2/2	70.0 – 130.7	3 – 2,196	[49, 55, 56, 58]
	12/13	13/13	16.7 – 194.6		
mTric	09/10	0/2	ND	<2 – 51	[63, 64]
	12/13	13/13	19.3 – 42.5		
Tric	09/10	1/2	225.9 – 248.5	10 – 5,370	[62]
	12/13	13/13	75.2 – 807.1		
BP-1	09/10	2/2	7.3 – 170.7	<2 – 41	[49, 59, 61]
	12/13	13/13	24.3 – 6832.2		
BPA	09/10	2/2	22.9 – 31.9	6 – 3,642	[22]
	12/13	13/13	4.7 – 985.7		
OMC	09/10	0/2	ND	<10 – 177	[56-58]
	12/13	0/13	ND		
E1	09/10	1/2	40.9 – 45.7	<0.1 – 147	[66, 67]
	12/13	11/13	3.1 – 331.6		
E2	09/10	0/2	ND	0.5 – 18	[54, 183]
	12/13	0/13	ND		
EE2	09/10	0/2	ND	<0.3 – 7.5	[65]
	12/13	7/13	11.5 – 77.8		
E3	09/10	0/2	ND	0.3 – 275	[54, 66, 187]
	12/13	0/13	ND		
Cstanol	09/10	NA	NA	10 – 200,000	[188]
	12/13	13/13	167.8 – 2697.3		

ND = not detected
NA = not yet an analyte at the time of analysis

4.3.3.2 2012/2013 Research Season

The nine most commonly detected target analytes in the Scott Base sewage effluents during the 2012/2013 season were OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, E1, and Cstanol. These analytes were detected in all samples, except for E1, which was not detected in the January and February effluent samples. These same analytes were also detected in the 2009/2010 Scott Base WWTP effluent samples, with the exception of methyl triclosan, which was not detected in 2009/2010. The WWTP samples collected in 2009/2010 were not analysed for faecal steroids. In addition to these nine analytes the target analyte EE2 was detected in all samples of the seven-day monitoring study in December, but was not detected in any other samples of Scott Base WWTP effluent. The results from the analysis of monthly Scott Base WWTP sewage samples collected over a period of six months, and the daily sewage samples collected over seven days are discussed in detail in separate sections below. The range and frequency of detected analytes are presented in Table 4.2 and are comparable to concentrations measured internationally in WWTP effluents (Table 4.2). The concentration range during the six month monitoring study lie in the mid to upper range of internationally measured sewage effluent concentrations. Analyte concentrations detected during the seven day monitoring study also lie in the mid to upper range of international data. However the effluent concentrations of OP, 4-MBC, BP-1, and EE2 were occasionally higher than those previously reported internationally (Table 4.2).

Results of the Monthly Monitoring Over a Full Research Season

The maximum Scott Base effluent concentrations of OP, 4-MBC, and methyl triclosan (4,066 ng L^{-1}, 2,126 ng L^{-1}, and 40.6 ng L^{-1} respectively) were close to the maximum concentrations observed internationally in WWTP effluents (3,949 ng L^{-1}, 2,300 ng L^{-1}, and 51 ng L^{-1} respectively, Table 4.2). The maximum concentration of BP-1 (461 ng L^{-1}) was an order of magnitude higher than previously reported for sewage effluent (41 ng L^{-1}). All other detected target analytes lie in the middle of previously reported international data ranges (Table 4.2). Measured target micropollutant concentrations for the individual samples are provided in Appendix B Table 9.8. The average concentrations of the nine commonly detected target analytes over the six-month sampling period are presented in Figure 4.6. None of the detected analytes correlated with the number of staff on base present at the time of sampling, or with the temperature of the WWTP. The data collected over the six months were not tested for seasonal effects due to the limited number of individual sampling events. Furthermore, the ozonation plant was in operation in January and February, but was out of service between August – December. This may have affected the concentration of detected analytes and therefore potentially caused a bias in the data.

The concentrations of most of the analytes varied from month to month. The largest concentration fluctuations in the Scott Base WWTP effluents occurred for OP, triclosan, and BP-1 (Figure 4.6). The concentrations of methyl triclosan and E1 remained relatively constant. The only target analytes demonstrating potential trends in effluent concentration were OP and 4-MBC. The effluent concentration of OP was highest at 4,066 ng L^{-1} in the August sample obtained before the start of the research season, before dropping to 496 ng L^{-1} in October and remaining relatively low throughout the remainder of the season. Conversely, 4-MBC concentrations increased steadily throughout the research season, increasing from 321 ng L^{-1} in August to 2,126 ng L^{-1} in January. Ozonation of the sewage effluent, which commenced in January, showed only minor, if any, effect on the concentrations of detected analytes, and is discussed in more detail in Section 4.3.3.3.

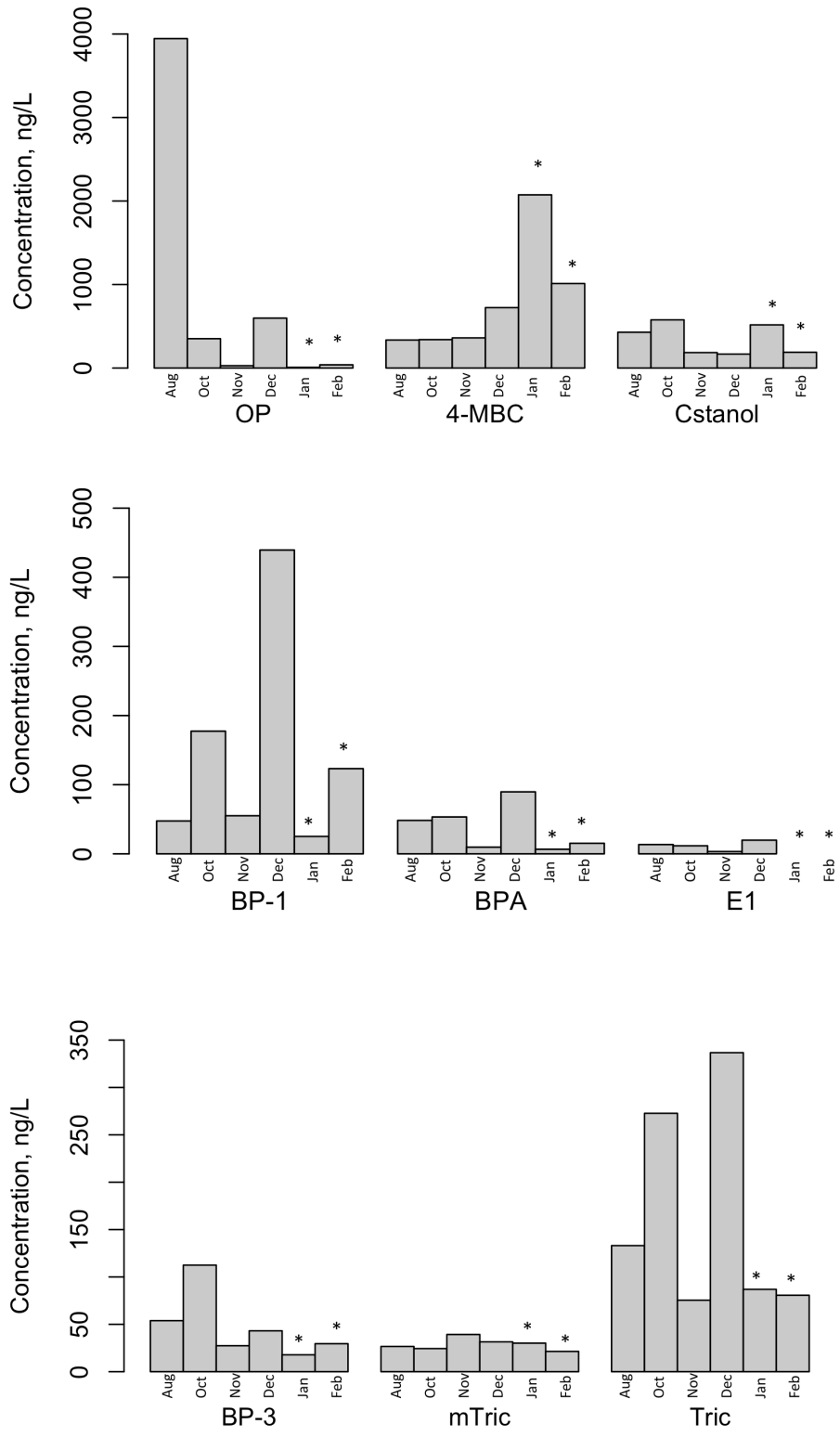


*Figure 4.6: Average monthly analyte concentrations (ng L^{-1}) of the nine most frequently detected analytes OP, 4-MBC, Cstanol, BP-1, BPA, E1, BP-3, methyl triclosan, and triclosan in Scott Base sewage effluents. Analytes were graphically arranged according to measured concentration ranges. * indicates when the ozonation plant was in operation.*

Results of the Daily Monitoring over a One Week Period

The average concentrations of the ten commonly detected target analytes measured in the Scott Base WWTP effluents over the period of one week are presented in Figure 4.7. The concentrations of OP, 4-MBC, BP-1, triclosan, BPA, and Cstanol increased over the 11 days since the December sample for the six-month study was collected, reaching a maximum concentration of 7,053 ng L^{-1}, 11,726 ng L^{-1}, 6,832 ng L^{-1}, 807 ng L^{-1}, 986 ng L^{-1}, and 2,697 ng L^{-1} respectively. These concentrations are also higher than those measured in any of the other samples collected during the six month study. In addition the target analyte EE2 was detected in the Scott Base effluents over this seven day period, despite not being detected in any other effluent samples from Scott Base or McMurdo. The analyte concentrations of each individual sample are provided in Appendix B Table 9.9. The maximum concentrations of OP, 4-MBC, BP-1, E1, and EE2 were higher than what has to date been reported internationally for sewage effluents (Table 4.2).

There was no consistent trend for the analyte concentrations. The concentrations of OP, triclosan, BPA, and EE2 increased over a 4 – 5 day period, before beginning to fluctuate during the remainder of the week. In comparison the effluent concentrations of 4-MBC, Cstanol, BP-3, and methyl triclosan remained relatively steady over the seven-day period. However 4-MBC and Cstanol spiked in concentration on the 5th and 7th sampling day respectively, while the concentrations of BP-3 decreased on the 6th and 7th of sampling. The concentration of BP-1 remained steady over the first three days of sampling before beginning to fluctuate during the last four days of sampling. The micropollutant concentrations did not correlate with the base population over the seven-day sampling period. However the faecal steroid Cstanol strongly correlated positively with base population (p = 0.00368). Base staff may not necessarily use PCPs such as sunscreens while on base unless they have to work outside for long periods of time.

The short-term variability of the concentrations of detected analytes (%RSDs) was highly variable. However, the long-term variability of analyte concentrations determined during the six-month study was found to be even more variable (Table 4.3).

Table 4.3: %RSDs of the concentrations of detected analytes during the six-month and seven-day monitoring study indicating the large observed concentration fluctuations.

	OP	4-MBC	BP-1	triclosan	BPA	E1	Cstanol	BP-3	Methyl triclosan	EE2
Long-term	178%	80%	102%	66%	84%	53%	52%	69%	21%	NA
Short-term	71%	50%	70%	19%	35%	42%	10%	32%	9%	50%

The maximum concentrations of OP and 4-MBC measured during the short term seven day study exceeded those measured during the six-month study. This demonstrates that field

studies conducted over long periods of time with low sampling frequencies can miss short-term concentration spikes of target analytes. The sudden appearance of EE2 in the effluents of Scott Base also demonstrates that long-term monitoring studies can miss the release of certain micropollutants and underestimate their environmental relevance. The temperature of the Scott Base WWTP remained constant at ~24°C over the week in which daily sampling was completed. The observed analyte concentration fluctuations are likely a reflection of the constantly and rapidly fluctuating volume and composition of influent entering the WWTP. The influent composition can be predominantly comprised of domestic grey water one day, and the next day become heavily influenced by waste streams from the mechanical workshops as a result of the design of the sewage system (Section 4.2.3.1). When science field parties return to base their field waste is also added to the WWTP, adding further pulses of waste. This could give rise to the unpredictable changes in pH and dissolved oxygen that have been reported by the Scott Base WWTP engineer, which in turn could affect the bacterial community and treatment efficiency of the WWTP.

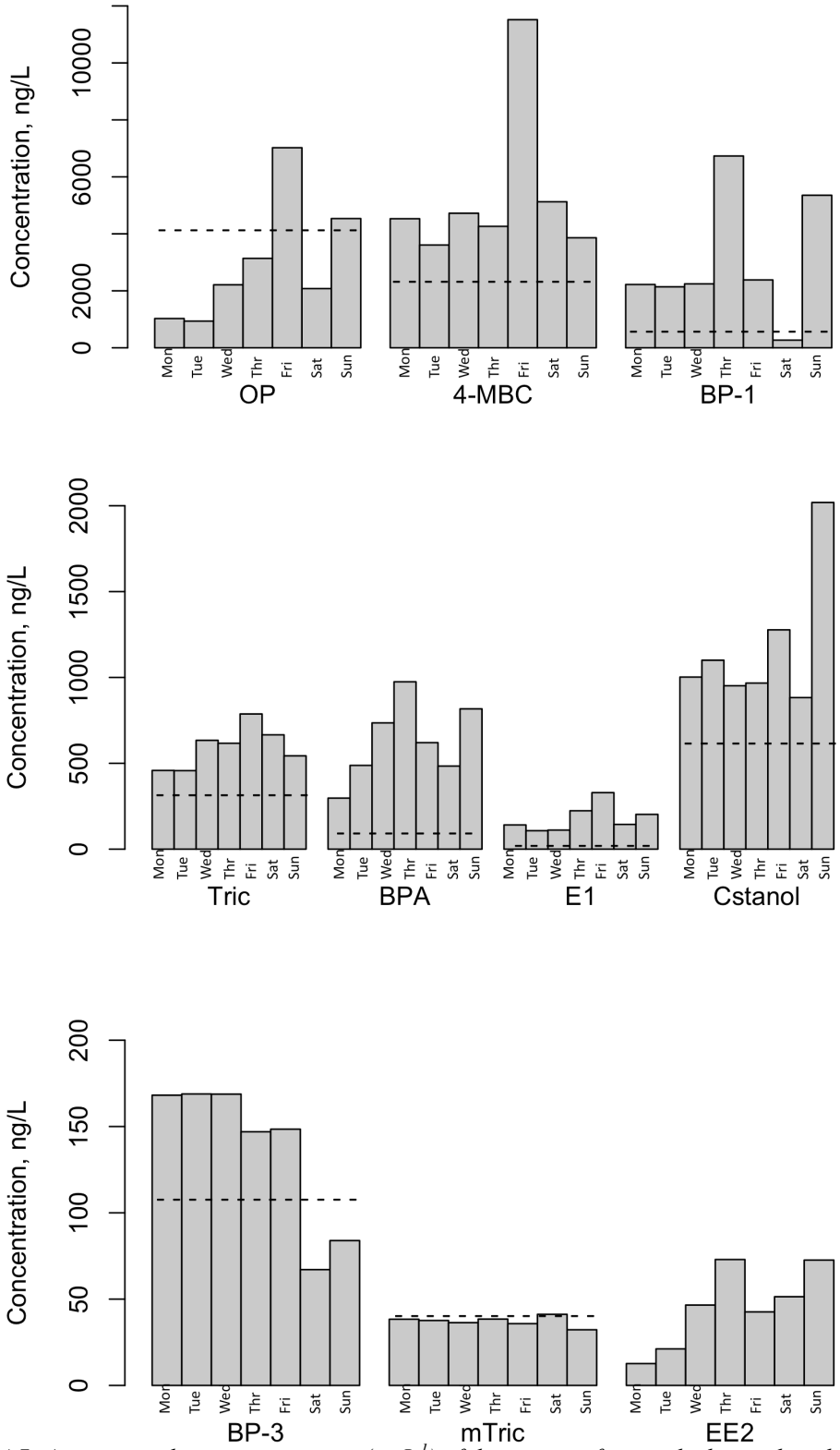


Figure 4.7: Average analyte concentrations (ng L^{-1}) of the ten most frequently detected analytes OP, 4-MBC, BP-1, triclosan, BPA, E1, Cstanol, BP-3, methyl triclosan, and EE2 in the Scott Base sewage effluents over a seven day sampling period in December 2012. Analytes were graphically arranged according to measured concentration ranges. Lines indicate maximum concentrations measured during the six-month study (except for EE2, which was not previously detected).

4.3.3.3 Effects of Ozonation on Effluent Concentrations of Micropollutants

During the 2012/2013 research season the ozonation plant was not operational until January 2013. As a result, ozonated sewage effluent samples were only obtained in the last two sampling months of January and February 2013. Due to the large concentration fluctuations of the detected target analytes observed over the previous four monthly sewage effluent samples it is difficult to discern whether the ozone treatment had any effect on the concentrations of the target analytes. The concentration of analytes detected in the January and February WWTP effluent samples were in the lower range of previously measured concentrations, but did not drop below the lowest measured concentrations obtained over the previous four months (Figure 4.6), with the exception of 4-MBC, which was highest in January and February. The concentrations of OP, BP-3, triclosan, and BPA were close to the lowest measured concentrations measured in November, and were comparable between January and February. The concentrations of Cstanol and BP-1 continued to fluctuate during January and February. Only E1 was completely removed from the sewage effluents in January and February.

A noticeable change in the colour of the sewage effluent samples was observed following commencement of ozone treatment. Sewage samples from August – December were a dark amber or tea colour, and became a light yellow colour in January and February. The dark colour of the sewage effluent suggests a high organic matter content. Ozone readily reacts with double bonds [257], thereby reducing the light absorbing properties of DOM. The effluent did not turn completely clear in January and February, suggesting a stoichiometric excess of organic matter with double bonds in the sewage effluent. This would leave only limited ozone available for the removal of organic micropollutants.

Further studies are required to investigate the effectiveness of ozonation on the removal efficiency of micropollutants in the sewage effluents of the Scott Base WWTP. While ozonation is efficient at oxidising dissolved organic matter (DOM) it has been postulated that the production of sufficient ozone for the complete degradation of DOM is not economically feasible due to the high DOM content of sewage effluent [257]. Due to this incomplete mineralization and the potential for ozonolysis to produce treatment by-products future research should investigate the toxicity of these by-products in addition to trace organic contaminants [257]. Furthermore, the majority of the knowledge on ozonation reactions come from empirical studies, which are costly and time consuming [258]. A new approach such as modelling is therefore called for [258].

With the exception of 4-MBC and OMC all target analytes in this study contained at least one –OH or –COOH group. Furthermore, all target analytes contained at least one double bond or

aromatic ring. The reactivity of organic compounds with oxidants such as ozone, chlorine, or chlorine dioxide depends on the environmental conditions and chemical properties of the organic compounds. Chemicals which can readily react with other oxidants such as chlorine can easily or even more easily react with ozone [258]. Deprotonated compounds react more readily than protonated compounds, so that ozone reactivity increases with increasing pH [8, 259]. This has for example been observed for the ozone mediated degradation of NP, BPA, E1, E2, EE2, and E3. [259, 260]. Molecular ozone is a selective electrophile which readily reacts with nucleophilic function groups and double bonds [257]. Organic compounds can be directly oxidised by ozone, or can react with the –OH radicals ozone gives rise to [182]. Ozone reactivity is more specific than that of –OH radicals, and reacts with specific functional groups in the order of thiols > amines > hydroxyls > carboxyls [8]. Similarly, aromatic double bonds are more reactive with ozone than aliphatic double bonds [8]. –OH radicals on the other hand are less selective, and can react faster than ozone [257]. However, –OH radical concentrations in natural waters are low [257], and –OH mediated degradation reactions are dependant on the amounts of DOM as DOM has a high –OH scavenging capacity [182]. For this reason advanced treatment processes combine ozone treatment with H_2O_2 to increase the production of –OH radicals [257]. The high concentration of DOM in the Scott Base sewage effluent may therefore decrease the effectiveness of –OH radical reactions, and may explain the limited decrease in the concentration of micropollutants following the reintroduction of ozonolysis of the Scott Base effluents.

Only E1 was removed to below the detection limit in the ozonated sewage effluents. The removal of steroid compounds with phenol groups such as E1, E2, and EE2 have been observed to be more than 98%, with lower removal observed for other steroids such as progesterone and testosterone [258]. At an ozone concentration of 2 – 9 mg L^{-1} the concentrations of the micropollutants BP-3, triclosan, E1, E2, EE2, and E3 were reduced by over 99% after two minutes of ozone residence time [257], with the majority of organic compounds reduced in surface and effluent waters at 0.5 mg L^{-1} and two minutes residence time [257]. Furthermore ozonation saw the estrogenicty of the sewage effluents drop by over 90% [257]. A second ozonation study also observed a decrease of estrogenicty to below the detection limit of the estrogenicity assay [261]. In this second study the concentrations of NP, BPA, and E2 were also reduced to below the detection limit with less than 0.5 mg L^{-1} ozone after 15 minutes [261]. A third ozonation study saw the concentrations of BP-3 and triclosan drop by 96% and 92% respectively [258]. However, advanced treatment processes can still not completely remove micropollutants in some treatment plants. The effluents of a Chinese treatment plant contained detectable levels of between <LOD – 7.4 ng L^{-1} of NP, OP, BPA,

E1, E2, and EE2 even after tertiary treatment which included coagulation-flocculation, continuous micro-membrane filtration, followed by ozonation [262].

4.3.4 Seawater

4.3.4.1 2009/2010 Research Season

A total of ten analytes were detected in Winter Quarters Bay and at Cape Armitage. The concentration range of detected analytes is provided in Table 4.4, and the concentrations for each individual sampling location are provided in Appendix B Table 9.5. All four UV filters, mParaben, pParaben, bParaben, OP, triclosan, and BPA were detected in the seawaters of Erebus Bay, at concentrations comparable to those reported for international coastal waters adjacent to significantly greater human populations (Table 4.4). This raises interesting questions with regards to why similar concentrations of these micropollutants occur in such vastly different environments (temperate vs. polar) with different population sizes. Unfortunately there are only limited literature data on the presence of the target analytes in coastal environments to answer this question, as previous research has primarily focused on fresh surface water systems such as rivers and lakes.

The maximum concentrations of 4-MBC, BP-3, BP-1, and OMC were 45.1, 88.4, 10.3, and 32.3 ng L^{-1} respectively in seawater, and were generally highest at Cape Armitage, located halfway between McMurdo and Scott Base. The UV filter 4-MBC was only detected in seawater sampled at Cape Armitage. The highest concentration of BP-3 was observed in seawater from Winter Quarters Bay. The concentration ranges for the UV filters reported in this study are comparable to those previously reported in coastal environments in other parts of the world [38, 39, 70, 71]. However, because studies on UV filters in the coastal environment are limited, the UV filters BP-1 and OMC have primarily been reported in samples obtained from recreational bathing sites. At these locations the levels of UV filters would be artificially elevated from indirect inputs via recreational activities [39, 70, 71]. 4-MBC, BP-3, and OMC have also been detected at trace levels in the surface microlayer in the Polynesian Pacific Ocean region [102]. Despite their high usage, relatively little is known about their environmental concentrations, primarily due to the lack of analytical methods [1].

All parabens except eParaben were detected in the seawater samples of Erebus Bay, albeit less frequently than the UV filters. Maximum concentrations of mParaben, pParaben, and bParaben were 33.3, 3.0, and 2.3 ng L^{-1} respectively in seawater. mParaben was detected most frequently, with pParaben and bParaben detected at only three locations. The highest concentrations of mParaben and bParaben were detected in seawater at Cape Armitage, while the highest concentration of pParaben was in seawater from Winter Quarters Bay. Only one

previous study could be found on the presence of parabens in a coastal environment, and the concentrations detected in Erebus Bay seawater fall within the same range [50] (Table 4.4). The widespread use of mParaben in PCPs [1, 111] is reflected in the Erebus Bay data as mParaben was the most commonly detected paraben in these coastal seawater samples.

OP was detected in all seawater samples from Erebus Bay, but at relatively low concentrations. The maximum concentration of 1.7 ng L^{-1} was measured at Cape Armitage, and the lowest concentration of 0.3 ng L^{-1} was at Winter Quarters Bay. Triclosan was detected in all but one seawater sample, with a maximum seawater concentration of 0.8 ng L^{-1} measured at Cape Armitage. The transformation product of triclosan, methyl triclosan, was not detected at any of the three sites. BPA was detected in all seawater samples, with a maximum BPA concentration of 31.1 ng L^{-1} measured in seawater from Cape Armitage. The concentrations of OP, triclosan, and BPA measured in Erebus Bay seawater lie within the range of concentrations (OP) or the lower end of the range (triclosan, BPA) reported internationally for coastal waters [22, 50, 62, 78, 79].

Similarly to the Whakaraupo Harbour study (Chapter 3) the paraben preservatives and OMC were frequently detected in the Erebus Bay seawaters but not in the sewage effluents of either McMurdo Station or Scott Base. Potential reasons for this are discussed in detail in Section 3.3.5. Unlike in Whakaraupo Harbour recreational activities can be ruled out as a potential source of the parabens and OMC in the Erebus Bay seawaters. However as described later in Section 4.2.3.2 tide-cracking is identified as a potential source of these micropollutants.

Table 4.4: Concentration range (ng L^{-1}) and comparison to literature values of target analytes in coastal seawater samples from the 2009/2010 and 2012/2013 Antarctic research season.

Analyte	Season	Frequency	Range	Literature range	Reference
mParaben	09/10	5/10	1.9 – 33.3	2.1 – 62	[50]
	12/13	39/48	<0.8 – 37.4		
eParaben	09/10	0/10	ND	<0.3 – 15	[50]
	12/13	0/48	ND		
OP	09/10	10/10	0.3 – 1.8	<0.04 – 800	[50, 77-79]
	12/13	2/48	0.4 – 0.9		
pParaben	09/10	3/10	<0.8 – 3.0	<0.5 – 7.9	[50]
	12/13	1/48	<0.8		
bParaben	09/10	3/10	<0.5 – 2.3	<0.2 – 7.1	[50]
	12/13	4/48	<0.5 – 0.7		
NP	09/10	0/10	ND	20.2 – 269	[50, 77-79,
	12/13	0/48	ND	<0.5 – 755	82, 179, 204]
4-MBC	09/10	1/10	45.1	13.1 – 798.7	[39, 70]
	12/13	38/48	<3.2 – 5.8		
BP-3	09/10	5/10	12.0 – 88.4	1. 8 – 3,300	[38, 70, 71]
	12/13	47/48	<2.6 – 3.7		
mTric	09/10	1/10	<0.2	NA	NA
	12/13	0/48	ND		
Tric	09/10	9/10	<0.5 – 1.7	0.008 – 39	[62, 73, 164]
	12/13	0/48	ND		
BP-1	09/10	7/10	<0.8 – 10.3	280	[71]
	12/13	0/48	ND		
BPA	09/10	10/10	2.2 – 29.5	<0.08 – 2,470	[50, 77-79,
	12/13	22/48	<1.3 – 5.7		82, 90, 131, 167, 168, 179, 180]
OMC	09/10	10/10	<1.9 – 32.3	7.4 – 389.9	[39, 70]
	12/13	44/48	<1.9 – 4.3		
E1	09/10	0/10	ND	0.08 – 103.9	[77, 82, 90,
	12/13	2/48	<7.0		168, 179]
E2	09/10	0/10	ND	0.4 – 175	[82, 168,
	12/13	0/48	ND		179, 180]
EE2	09/10	0/10	ND	0.14 – 101.9	[77, 82, 90,
	12/13	2/48	<1.4		179, 180]
E3	09/10	0/10	ND	ND	[77, 82, 164]
	12/13	1/48	<2.0		
Cstanol	09/10	NA*	NA*	<10 – 47,500	[210]
	12/13	0/48	ND		

ND = not detected
NA = no literature data available
NA* = not yet an analyte at the time of analysis

4.3.4.2 Cape Evans Reference Site, 2009/2010 Research Season

Unexpectedly, the majority of compounds (seven out of ten) which were detected in seawater in close proximity to the research stations were also detected in seawater at the Cape Evans reference site, located 25 km north and up-current from the primary sampling area. The area down-current from the research stations could not be sampled as it is covered by the floating edge of the Ross Iceshelf which could not be drilled through due to its thickness. Eight analytes, BP-3, OMC, mParaben, pParaben, OP, triclosan, BPA, and the transformation

product of triclosan, methyl triclosan, which was not detected at any other location, were detected in Cape Evans seawater (Appendix B Table 9.5). The concentrations of the detected analytes at Cape Evans were generally lower than those measured in seawater closer to the research stations. However the concentration of BP-3 and OP in Cape Evans seawater (29.9 ng L^{-1} and 0.5 ng L^{-1} respectively) exceeded the concentration measured in seawater near the sewage outfall of McMurdo Station at WQB location 1 (23.7 ng L^{-1} and 0.4 ng L^{-1} respectively). Triclosan and methyl triclosan concentrations at Cape Evans were below the limit of quantification (0.5 ng L^{-1} and 0.2 ng L^{-1} respectively). No previous studies reporting the presence of methyl triclosan in coastal seawater could be found for comparison. However, concentrations of methyl triclosan of up to 2 ng L^{-1} have been reported in lake water [63], and at 5 ng L^{-1} in river water [89]. There is limited data on the presence of methyl triclosan in the environment [99] as it is detected less frequently than triclosan [62].

Cape Evans lies approximately 25 km north from the Scott Base and McMurdo WWTP discharge points. Cape Evans was selected as a reference site because of this distance from the research bases. The detection of target analytes in seawater at this location is a cause for concern, and shows that the sources and distribution mechanisms of sewage derived pollutants in the marine environment are not yet fully understood. The ocean currents in Erebus Bay predominantly flow from Cape Evans towards Scott Base and McMurdo Station. However some re-circulation of the water within Erebus Bay does occur due to the complex topography of the region [247, 248]. Some pockets of diluted effluent water may therefore have the potential to drift around Erebus Bay and up to Cape Evans. As discussed in Section 4.2.3.2 the tide-cracking of sewage and grey water may also be a source of micropollutants at sites of human activity far removed from the research stations. The occurrence of micropollutants in Cape Evans seawater suggests a much wider area of Erebus Bay is affected by human sewage waste than was previously thought.

4.3.4.3 2012/2013 Research Season

To gain a better understanding of the distribution and temporal variability of micropollutants in Erebus Bay a more comprehensive field study was carried out over the 2012/2013 summer research season. The target analytes detected in the Erebus Bay seawaters during this research season were similar to those detected during the 2009/2010 research season. Eleven analytes were detected in the seawaters, namely mParaben, pParaben, bParaben, OP, 4-MBC, BP-3, BPA, OMC, E1, EE2, and E3. The concentration ranges for the detected analytes are provided in Table 4.4 along with a comparison to the 2009/2010 data and data previously reported internationally for coastal waters. The most commonly detected analytes were mParaben, 4-MBC, BP-3, BPA, and OMC. The less commonly detected analytes OP, EE2, and E3 were

only detected in seawater from close to the research stations, while pParaben and bParaben were detected further away. EE2 and E3 were only detected once in Winter Quarters Bay seawater, directly off the coast of McMurdo Station. Detected concentrations from each sampling location and sampling round are provided in Appendix B Table 9.12 and summarized in Figure 4.8.

The detected seawater concentrations were lower in 2012/2013 compared to 2009/2010, and fall into the lower range of concentrations reported in the international literature (Table 4.4). There are two possible explanations to this observation. Firstly, the sea ice in Erebus Bay had broken out in early 2012 for the first time in over 13 years [263, 264]. Secondly, the field work completed over the 2012/2013 season was carried out later in the season than in 2009/2010. Changes in irradiance levels, coupled with different sea ice conditions may have affected the concentrations of micropollutants in the Erebus Bay seawater. Similar to 2009/2010 the analytes mParaben and OMC were detected in most seawater samples, but not the sewage effluents discharged from Scott Base. The concentrations of the most commonly detected analytes mParaben, 4-MBC, BP-3, BPA, and OMC were distributed evenly throughout Erebus Bay. This suggests the seawater is well mixed, but that limited dilution of the sewage effluents occurs as it becomes distributed across Erebus Bay towards Cape Evans. Consequently the concentration of detected analytes did not differ between sampling rounds, except for BPA concentrations, which were slightly elevated in Round 1 compared to Round 2 (paired t-test, $p = 0.026$).

The only contaminant demonstrating a concentration gradient in the seawaters was mParaben, which increased in concentration from Site 14 (12 ng L^{-1}) to Sites 11 (37 ng L^{-1}) and 8 (31 ng L^{-1}) (Appendix B Table 9.12). This pattern is of interest as these concentrations were the highest recorded for any analyte in Erebus Bay during the 2012/2013 sampling round. Similarly, during sampling Round 1 the concentrations of mParaben at Sites 14, 11, and 8 were 6 ng L^{-1}, 3 ng L^{-1}, and 6 ng L^{-1} respectively, which were the highest concentrations of mParaben recorded during Round 1. This distribution pattern for mParaben suggests the area of Erebus Bay between McMurdo Station and the Erebus Ice Tongue is an area where sewage derived micropollutants may become trapped. The concentration patterns of mParaben suggests a trail of sewage effluent was sampled in Round 2 as it drifted north from McMurdo Station and became trapped by the Erebus Ice Tongue. Following seawater extraction, the SPE cartridges from Sites 14, 11, and 8 were also more discoloured than those from other sites, indicating these seawater samples contained higher quantities of dissolved organic matter. The seawater samples from sites 11 and 8 were also the only two samples of the whole study at which E1 was detected, providing further evidence that a pocket of sewage was sampled. Seawater from site 8 was sampled on the first day of sampling for Round 2, while

the seawaters from sites 11 and 14 were sampled on the second day. Only a small difference in the concentration of mParaben was observed between Site 8 and 11, which are located in the same geographical sampling area (Figure 4.8), suggesting that over the course of 24 hours only limited dilution occurs and that the velocity of the current flow was low. Interestingly the concentrations of all other detected analytes at sites 8, 11, and 14 were not elevated compared to the other sites of this study in Erebus Bay.

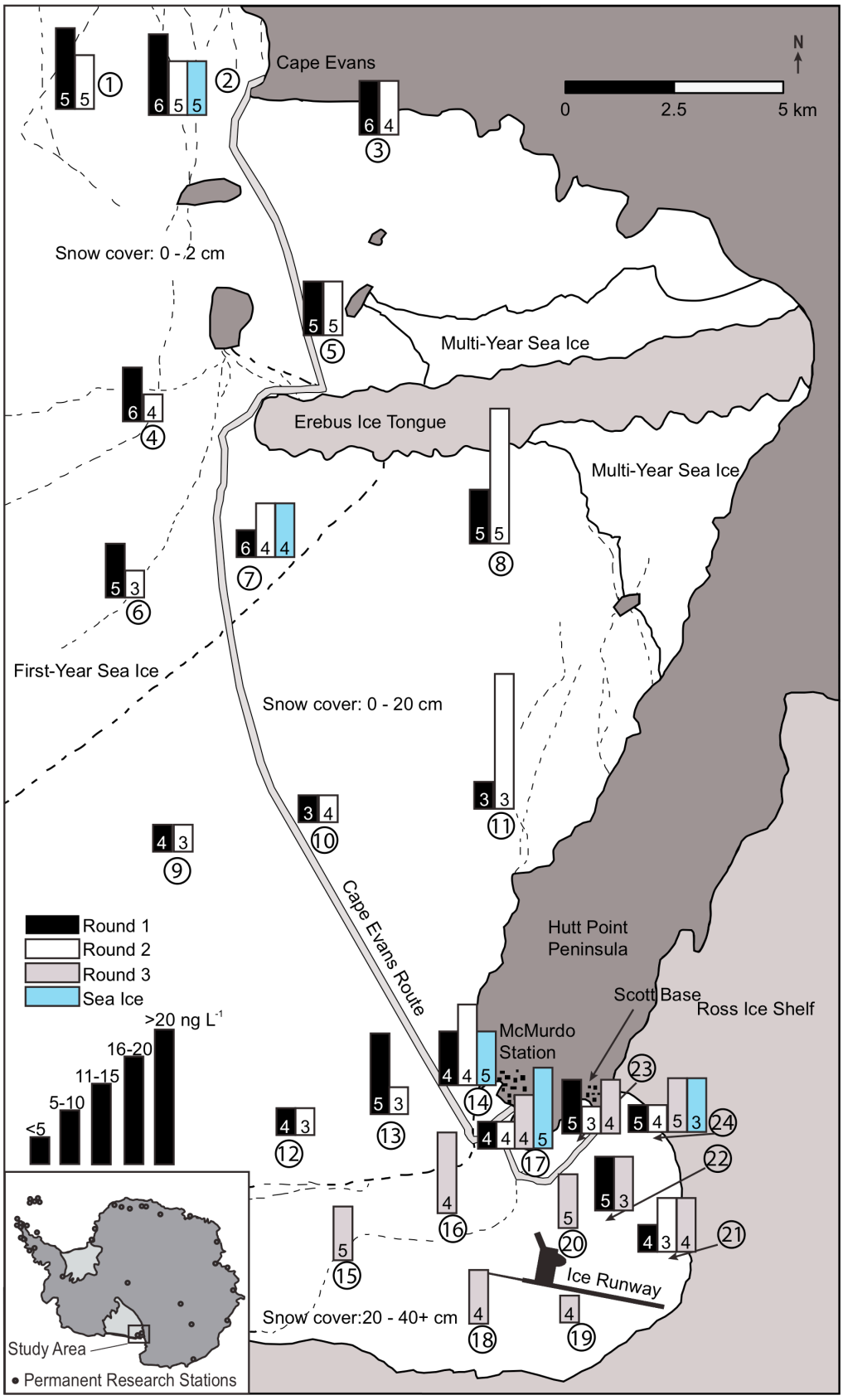


Figure 4.8: 2012/2013 study area and distribution of detected target analytes at each sampling location. Sampling locations are indicated by the circled numbers. The height of each bar shows the total concentration burden of micropollutants at each site for each of the three sampling rounds (distinguished by colour). The number inside each bar indicates the number of detected target analytes.

4.3.4.4 Sea Ice Water

The potential for sea ice to act as an environmental sink and potential source of micropollutants within Erebus Bay was investigated by determining the concentration of micropollutants present in Erebus Bay sea ice. The concentration range of target analytes detected in the sea ice is provided in Table 4.5. Because no data exists on the occurrence of micropollutants in sea ice the detected concentrations were compared to previous reports of their concentration in seawater. The concentrations detected in sea ice from each of the five sampling locations are provided in Appendix B Table 9.13. The data for each sampling location and sampling round are also included in Figure 4.8.

A total of seven target analytes were detected in the sea ice, namely OP, 4-MBC, BP-3, BPA, OMC, E1, and EE2. With the exception of OP, E1, and EE2 these were also the most commonly detected target analytes in the seawater within Erebus Bay (Table 4.5). However mParaben was an exception as it was not detected in the sea ice, despite being frequently detected in the seawater. The concentration range of the detected target analytes in the sea ice samples is comparable to that detected in the corresponding seawater samples (Figure 4.8).

Table 4.5: Concentration range (ng L^{-1}) and comparison to seawater literature values of target analytes in thawed sea ice from the 2012/2013 Antarctic research season.

Analyte	Frequency	Range	Literature Range	Reference
OP	2/5	0.5 – 0.9	<0.04 – 800	[50, 77-79]
4-MBC	5/5	<3.2 – 4.3	13.1 – 798.7	[39, 70]
BP-3	5/5	<2.6 – 3.8	1. 8 – 3,300	[38, 70, 71]
BPA	2/5	<1.3	<0.08 – 2,470	[50, 77-79, 82, 90, 131, 167, 168, 179, 180]
OMC	5/5	<1.9 – 4.8	7.4 – 389.9	[39, 70]
E1	2/5	<7.0	0.08 – 103.9	[77, 82, 90, 168, 179]
EE2	1/5	<1.4	0.14 – 101.9	[77, 82, 90, 179, 180]

This data demonstrates that sea ice can act as a sink of micropollutants. These micropollutants present in the sea ice will have likely been present in seawater during the previous research season and become entrapped in the sea ice as it re-formed during autumn and winter [243, 265]. During the following season these micropollutants would be released back into the seawater as the ice melts during summer. The sea ice may also transport these micropollutants to previously un-impacted areas when it breaks out and is transported away by the ocean currents. Large otherwise isolated areas of the aquatic environment may therefore be exposed to seasonal pulses of sewage-derived micropollutants.

Previous work in the Arctic environment demonstrated the accumulation of the organic contaminant hexachlorocyclohexane (HCH) in the brine and ice crystal matrix of the sea ice [266], though HCH generally associated with the brine fraction [266]. Once the brine fraction of the ice increased to over 5% the brine was rejected from the sea ice, carrying with it the

concentrated HCH, and thereby increasing the HCH concentrations in the seawaters below the sea ice [266]. Given the large extend of sea ice cover in the polar regions of the globe further studies on the dynamic interactions between sea ice and environmental contaminants are warranted [266].

4.3.5 Biota

As was previously experienced in the analysis of mussels from Whakaraupo Harbour (Section 3.3.7), matrix interferences prevented the detection and/or quantification of a number of spiked surrogates and spiked analytes from the fish, clams, and the urchin composite. However the mass spectral chromatograms of the Antarctic biota were considerably cleaner, and more compounds could be identified compared to the Whakaraupo Harbour mussels. The surrogates $^{13}C_6$-mParaben, $^{13}C_6$-bParaben, and $^{13}C_6$-E2, and the analytes mParaben, eParaben, pParaben, bParaben, OP, BP-3, BP-1, E1, E2, EE2, E3, and Cstanol could be adequately quantified in the biota samples from Erebus Bay.

Table 4.6: Concentration range and comparison to literature values of detected target analytes in Antarctic clams, urchins, fish, and fish liver obtained during the 2009/2010 research season. Concentrations are reported in ng g^{-1} wet weight (w.w.), ng g^{-1} dry weight (d.w.), and ng g^{-1} lipid weight (l.w.) to allow for comparisons with the literature [a].

		Clams (n=7) and Urchin composite (n=10)		Fish (n=7) and Fish Liver		Biota Literature	
Analyte		**Range (Frequency)**	**Urchin**	**Range (Frequency)**	**Fish Liver**	**Literature Range**	**Ref**
mParaben	d.w.	<2.1 – 5.8 (7)	5.7	5.1 – 26.9 (7)	2.4	0.86 – 2.3 μg g^{-1} w.w.	[113]
	w.w	<0.4 – 1.0	0.6	1.0 – 6.1	0.3		
	l.w.	*	*	202.4 – 1,985.5	100.4		
OP	d.w.	–	–	1.6 – 5.0 (7)	–	2.7 – 18.6 μg kg^{-1} w.w	[224]
	w.w.			0.3 – 1.1		6.7 – 44.9 ng g^{-1} w.w	[131]
	l.w.			63.9 – 464.1		3190 – 4920 ng g^{-1} l.w.	[201]
pParaben	d.w.	2.1 – 5.3 (4)	–	–	–	0.87 – 6.7 μg g^{-1} w.w.	[114]
	w.w.	0.4 – 1.9					
	l.w.	*					
BP-3	d.w.	9.2 – 112.0 (7)	8.6	<6.6 – 14.1 (7)	41.0	11.2 – 24.3 ng g^{-1} d.w.	[225]
	w.w.	1.4 – 23.1	0.9	<1.3 – 3.0	9.6	22 – 298 ng g^{-1} l.w.	[103]
	l.w.	*	*	264.8 – 1454.2	1689.8	<50 – 151 ng g^{-1} l.w.	[83]
						66 – 123 ng g^{-1} l.w.	[56]
E2	d.w.	5.1 – 10.9 (3)	–	–	–	NA	NA
	w.w.	0.8 – 2.0					
	l.w.	*					
EE2	d.w.	8.1 – 23.1 (4)	–	–	–	<3 – 38 ng g^{-1} d.w.	[82]
	w.w.	1.5 – 4.3					
	l.w.	*					
Cstanol	d.w.	76.2 – 229.6	1255.4	–	–	NA	NA
	w.w.	(5)	133.3				
	l.w.	9.4 – 35.9	*				
		*					

[a] biota reference values include fish and shellfish
NA = no literature data available
*fat content of the biota tissue was too low to be accurately determined gravimetrically.

In total six analytes and the faecal steroid coprostanol could be detected in the biota from Erebus Bay (Table 4.6). The analytes concentrations are reported by dry weight (d.w.), wet weight (w.w.), and lipid weight (l.w.) to allow for easier comparison to previous studies. Lipid contents of the clams and urchin composite were too low to be determined accurately by gravimetric methods. Tissue concentrations for these samples are therefore only reported on a dry weight and wet weight basis. The lipid content of the fish tissues was also low as the fish were caught in the beginning of spring when they are just beginning to feed after a long period of starvation during winter [267]. The reported lipid based concentrations are therefore elevated and need to be carefully during comparisons to previous studies.

The clams obtained from Winter Quarters Bay off the coast of McMurdo Station contained up to 5.8, 5.3, 112.0, 10.9, and 23.1 ng g^{-1} d.w. of mParaben, pParaben, BP-3, E2, and EE2 respectively. The sea urchin composite, obtained from Cape Armitage between McMurdo Station and Scott Base, contained 5.7 and 8.6 ng g^{-1} d.w. of mParaben and BP-3 respectively. The sewage exposure indicator coprostanol could also be detected in five out of seven analysed clams, and the urchin composite. Interestingly, the fish, obtained 25 km away from the two research stations, contained up to 19.2, 5.0, and 14.1 ng g^{-1} d.w. of mParaben, OP, and BP-3 respectively. It has been demonstrated that *Trematomus bernachii* do not migrate beyond 500 meters of their point of release after tagging [267]. Micropollutants are therefore likely to be continuously present in the seawaters at Cape Evans tin order for them to bioaccumulation in these fish. The fish liver also contained 2.4 and 41.0 ng g^{-1} d.w. mParaben and BP-3 respectively. These mParaben and BP-3 concentrations are the lowest and highest respectively of all the fish tissues. This suggests the liver does not accumulate mParaben and OP, but does accumulate BP-3, compared to the fish muscle tissue.

There is limited international field data reporting these micropollutants in aquatic biota (Table 4.6). In laboratory based fish exposure studies have demonstrated the dose-dependant accumulation of mParaben in the gill, liver, muscle, brain, and testis tissues of *Cyprinus carpio* [113]. At an aqueous exposure of 1.68 mg L^{-1} mParaben accumulated in *Cyprinus carpio* in gill, liver, muscle, brain, and testis tissues to 0.86 μg g^{-1}, 1.7 μg g^{-1}, 0.88 μg g^{-1}, 2.3 μg g^{-1}, and 1.4 μg g^{-1} respectively [113]. A second laboratory based fish exposure study on *Oncorhynchus mykiss* demonstrated a 12-day exposure to 225 μg L^{-1} pParaben resulted in concentrations of 6.7 μg g^{-1} and 0.87 μg g^{-1} in liver and muscle tissue respectively [114]. The half-lives of pParaben in fish liver and muscle tissues were 8.6 hours and 1.5 hours respectively [114].

The concentration of OP detected in the Cape Evans fish (0.3 – 1.1 ng g^{-1} w.w.) lies in the lower ranges of concentrations reported in aquatic biota (2.7 – 44.9 ng g^{-1} w.w.) [131, 224].

Bioaccumulation of OP in fish has been reported [100]. While OP can be metabolized and excreted via the liver/bile route by fish, OP has been shown to accumulate in fish brain, muscle, skin, bone, gill, and eye tissue [268] One previous study has reported the occurrence of OP in fish, at a concentration range of 31.4 ± 15.0 (n=5) ng g^{-1} w.w. [131]. The lipid based concentration range of OP in the Antarctic fish (63.9 – 464.1 ng g^{-1} l.w.) is also much lower than has been detected in shellfish (3190 – 4920 ng g^{-1}) [201].

The measured dry weight based concentration range of BP-3 (4.7 – 112.0 ng g^{-1} d.w.) is higher than has previously been reported in fish (11.2 – 24.3 ng g^{-1} d.w.) [225]. There is an almost 5-fold difference between the maximum values of this study and available literature for BP-3. The lipid based BP-3 concentration ranges in the Cape Evans fish (264.8 – 1454.2 ng g^{-1} l.w.) are equally elevated compared to previous studies in fish from around the world (<50 – 298 ng g^{-1} l.w.) [56, 83, 103, 159, 225]. This is likely in part due to the fact that the Antarctic fish lipid contents were low after the starvation period during winter. If fish were caught at the end of the Antarctic summer the lipid based concentrations of all detected analytes would likely be lower. The concentrations of EE2 measured in the clams (8.1 – 23.1 ng g^{-1} d.w.) lie in the same range as reported in mussels (<3 – 38 ng g^{-1} d.w.) from a lagoon in Venice [82].

Most interestingly, the concentrations of mParaben reported in the Cape Evans fish correlated negatively with fish fillet weight (Pearson Correlation, R = 0.66126 , *p*-value = 0.02612)(Figure 4.9). This is evidence of growth dilution, the phenomena where tissue concentrations fall as a result of the same quantity of material being distributed in a larger volume of tissue [269, 270]. Growth dilution can be especially significant if other clearance rates such as metabolism or faecal extraction rates are low [269].

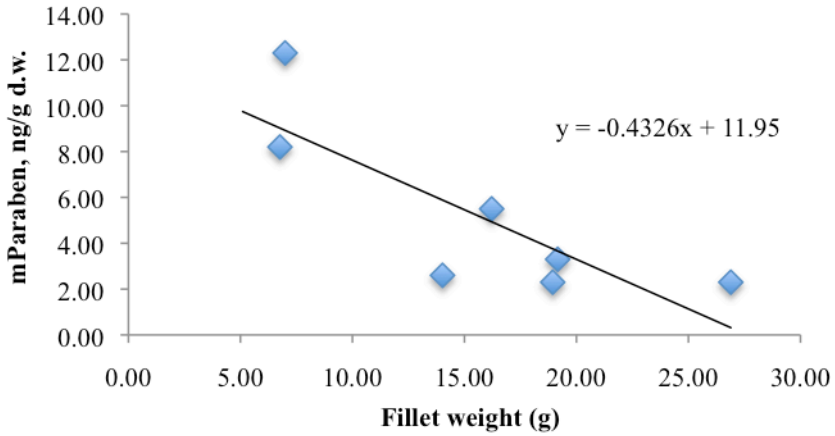


Figure 4.9: Linear regression of mParaben concentration (ng g^{-1} d.w.) against fish fillet size (g) (R^2 = 0.6613, p =0.026).

Trematomus bernachii have a unique growth cycle due to the unique Antarctic environment. Between the months of May and September the fish stop growing, but instead lose weight as

food becomes scarce during winter. At the onset of spring when food again becomes available the fish begin to eat to recover their lost body weight. By December the fish resume their growth until April, at a rate of 30 – 40 mm p.a. for fish below 150 mm in length, and 15 – 20 mm p.a. in fish above 150 mm in length. Spawning occurs in early spring for sexually mature adults [267].

Bioaccumulation is the net result of competing rates of accumulation and elimination processes which can change throughout the life time of an organism [229], and can be mathematically expressed using equation (2),

$$BAF = \frac{\{k_1 + k_2(C_{biota}C_{aq})\}}{k_3 + k_4 + k_5 + k_6} \quad (2)$$

where C_{biota} = concentration of analyte in biota, C_{aq} = concentration of analyte in the aqueous phase, k_1 = gill uptake, k_2 = dietary uptake, k_3 = gill elimination, k_4 = fecal egestion, k_5 = metabolic transformation, and k_6 = growth dilution [229].

Over this annual starvation–feeding–growth cycle these various processes recede or become dominant. During the starvation period the mobilization of fat likely releases mParaben into the blood where it could enter into enterohepatic recirculation, the process whereby compounds are continuously recycled between the blood, liver, gall bladder, and intestines [271]. This has been shown to occur in perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*) [271]. Some mParaben may therefore be metabolized as it passes through the liver and is removed from the fish. mParaben may also be deposited into the roe during this time of the year as spawning occurs at the beginning of spring. During the feeding and growth phases in summer the deposition of fat and the possible ingestion of mParaben containing food then replenishes the lost mParaben.

This evidence for bioaccumulation of mParaben and pParaben is unexpected due to their low log K_{OW} values of 1.66 and 2.71 respectively [34], and their low log K_{OC} of 2.35 and 2.89 respectively (Table 1.4), and are therefore not expected to bioaccumulate in the environment. However, other mechanisms such as partitioning into non-water and non-lipid cellular components of the organism may play a role in bioaccumulation [228]. These mechanisms include active transport processes instead of diffusion processes, and sorption to proteins [228]. This bioaccumulation may also be highly species and compound specific, and may not occur in other Antarctica biota. For example, the bioaccumulation of various classes of organchlorine chemicals has been previously observed to be species specific [272, 273]. Furthermore, the accumulation of BP-3 in the fish did not correlate with fish size, and no accumulation trends were observed in the clam tissue for any anlaytes.

As for the Whakaraupo Harbour biota data (Chapter 3, Section 3.3.7) a simple concentration factor for the clams, urchin composite, fish muscle, and fish liver tissues was calculated using equation (1),

$$CF = \frac{C_{biota}}{C_{aq}} \qquad (1)$$

where C_{biota} = wet weight concentration of analyte in biota, C_{aq} = concentration of analyte in the aqueous phase from the 2009/2010 field study data. Estimated concentration factors are provided in Table 4.7. Where target analytes were detected in the biota but not the seawater (OP for the fish, and E2 and EE2 for the clams) a seawater concentration of half the LOQ was used.

Table 4.7: Estimated concentration factors of detected target analytes in clam, urchin, fish, and fish liver tissue.

Analyte	Clams	Urchin	Fish	Fish Liver
mParaben	15 – 160	18	530 – 3,200	160
OP	–	–	3,000 – 11,000	–
pParaben	130 – 630	–	–	–
BP-3	35 – 585	15	35 – 100	330
E2	4,000 – 10,000	–	–	–
EE2	2,140 – 6,140	–	–	–

The concentration factors of mParaben were higher in fish tissues (530 – 3,200) than clams (15 – 160) and the sea urchin composite (18). This is because the aqueous concentrations of mParaben were higher at the collection sites of the clams (Winter Quarters Bay) and urchins (Cape Armitage) than for the fish (Cape Evans). The larger the water concentration in equation 1 becomes the smaller the concentration factor becomes. Similarly, the high aqueous concentration of BP-3 in Winter Quarters Bay has resulted in a low concentration factor for the clams (130 – 630). The high concentration factors for OP in fish (3,000 – 11,000), E2 in clams (4,000 – 10,000), and EE2 in clams (2,140 – 6,140) were due to the low aqueous concentrations at the sampling sites. BCFs of OP in fish have been estimated to range between 267 – 471 [100], which is orders of magnitude lower than those calculated in this study. BCFs of EE2 in mussels have been calculated to range between 1,300 – 1,500 [82], which are also lower than those reported in this study, but are in the same order of magnitude. The BAF of E2 and EE2 have also been modelled in plankton, invertebrates, and fish, and were estimated at 152, 326, and 61 respectively for E2, and 70, 186, and 332 respectively for EE2 [274]. To our knowledge no BCF or BAF values are available for mParaben, pParaben, and BP-3, though BP-3 has been shown to bioaccumulate [56, 83, 103]. The aqueous concentrations of mParaben, pParaben, and BP-3 have decreased in the 2012/2013 season compared to 2009/2010. The concentration factors of these contaminants may also have

changed since the biota samples were collected in the 2009/2010 season. Future sampling and analysis of biota over a number of seasons is necessary to confirm these preliminary results and determine the pattern of accumulation of these chemicals within biota in Erebus Bay.

4.4 Comparison to Whakaraupo Harbour

The data obtained during the two Antarctic case studies compares well with the data obtained from the Whakaraupo Harbour study in New Zealand. The most frequently detected target analytes in the Scott Base sewage effluents (OP, 4-MBC, Cstanol, BP-1, BPA, E1, BP-3, methyl triclosan, and triclosan) were also the compounds most commonly detected in the effluents of the three Whakaraupo Harbour WWTPs. Only EE2 was the only additional micropollutant detected in the Scott Base effluents, but only during the seven-day monitoring study. With the exception of BP-3 and methyl triclosan the concentration ranges of all detected analytes were considerably higher in Scott Base WWTP effluent compared to Whakaraupo Harbour WWTPs effluents. The month-to-month fluctuations in the concentrations of the detected micropollutants were also greater in the Scott Base sewage effluent, and showed little or no temporal trends, similar to those observed in the effluents of the Whakaraupo Harbour WWTPs. This can be explained by the much greater and faster environmental changes the Scott Base WWTP is subjected to. Only minor comparisons can be made with the data from the McMurdo WWTP sewage effluent due to the small sample size. The low concentrations and limited number of target analytes detected in the McMurdo sewage effluents (BP-3 and BP-1, and BPA) suggests a high level of treatment is achieved, even compared to the Whakaraupo Harbour WWTPs.

The data obtained from the seawater samples of Erebus Bay compares well with the Whakaraupo Harbour study. Only limited data trends were observed. Concentrations of target analytes in Erebus Bay did not correlate with sampling location or with each other for all sampling rounds. Only BPA concentrations significantly differed between sampling Rounds 1 and 2 in Erebus Bay (paired t-test, $p = 0.02578$). As in Whakaraupo Harbour, the micropollutants mParaben and OMC were frequently detected in the seawaters of Erebus Bay, but not in the sewage effluents discharged into the coast. As was proposed in the Whakaraupo Harbour study, conjugation of the parabens during wastewater treatment and subsequent cleavage after release of paraben preservatives may be a potential source. Tide-cracking may be a source of the paraben preservatives and OMC specific to Erebus Bay and not Whakaraupo Harbour. The sewage effluents of McMurdo station may also be a significant source of these micropollutants in the seawaters of Erebus Bay.

A greater number of target analytes were detected in the Antarctic biota compared to the New Zealand mussels. The Antarctic urchin composite contained mParaben, BP-3, and Cstanol.

The fish contained mParaben, OP, and BP-3. The clams contained six target analytes, namely mParaben, pParaben, BP-3, E2, EE2, and Cstanol. Only mParaben, OP, and BP-3 were detected in the New Zealand mussels. This is most probably a reflection of the reduced matrix interferences encountered during the analysis of the Antarctic biota samples compared to the New Zealand mussels. The concentrations of mParaben and OP were comparable between the Antarctic and New Zealand biota, while the concentration of BP-3 in the New Zealand samples was lower than in the Antarctic biota. mParaben was detected in all New Zealand and Antarctic samples. OP was detected in all but two New Zealand mussel samples, but was only detected in the Antarctic fish tissues. Lastly, BP-3 was detected in only one New Zealand mussel composite, but was detected in all Antarctic samples. The concentration factors of mParaben for the Antarctic and New Zealand biota were of the same order of magnitude, but were higher in the New Zealand mussels (2,200 – 8,400 compared to 530 – 3,200). The concentration factors of OP were also in the same order of magnitude, but higher in the Antarctic biota than the New Zealand biota (3,000 – 11,000 compared to 1,800 – 3,800). Lastly, the concentration factor based on the single detection of BP-3 in the New Zealand mussel was higher than that in the Antarctic biota (6,400 compared to 35 – 585).

4.4.1 Environmental Implications

Based on the comparable range of detected analytes and concentrations in the sewage effluents, seawaters, and biota of Whakaraupo Harbour and Erebus Bay the potential environmental implications discussed in Chapter 3 also apply to the Antarctic environment. The widespread detection of micropollutants across Erebus Bay indicates a large coastal area is affected by anthopogenic influences. As discussed in Chapter 3 the concentrations of the micropollutants detected in Erebus Bay seawater are below those at which biological effects have been observed. However these aqueous concentrations were sufficient to raise the sediment concentrations of micropollutants in Whakaraupo Harbour to biologically active levels. While sediment samples could unfortunately not be obtained in the Antarctic case study, similar concentrations of these micropollutants may accumulate in the sediments of Erebus Bay.

The human faecal steroid marker Cstanol has previously been detected in sediments of WQB and Cape Armitage [275]. The concentrations of up to 1.5 mg Cstanol g^{-1} organic carbon were comparable to those detected in sediment samples at urban sewage outfalls worldwide [275]. It is plausible that micropollutants present in the seawater of Erebus Bay could similarly partition directly into, and accumulate within, the sediments of Erebus Bay. In comparison to seawater samples from Whakaraupo Harbour the Erebus Bay seawater samples were observed (from filtering the water priot to SPE extraction) to contain very few suspended materials

which would help facilitate the accumulation of micropollutants into the sediments. Cstanol was detected in all sediment samples collected from Whakaraupo Harbour, and the sediments were found to act as a sink for micropollutants. The same situation may occur in Erebus Bay. Indeed the analysed bottom dwelling clams and urchins from Erebus Bay were found to accumulate mParaben, pParaben, BP-3, E2, EE2, and Cstanol. This may be in part due to their close proximity to the sewage outfalls of McMurdo Station and Scott Base, but possibly also due to them being sediment dwelling organisms. Fish obtained 25 km away from these sewage outfalls were also found to accumulate mParaben, OP, and BP-3. It is therefore likely the majority of aquatic organisms within Erebus Bay will be similarly exposed to, and accumulate, these micropollutants. The wide distribution of organic contaminants has been previously observed in Erebus Bay [146]. A survey of polybrominated diphenyl ether flame retardants (PBDEs) in the clams *Laternula elliptica* and the fish *Trematomus bernachii* (the same species used here) found detectable concentrations of PBDEs in these biota tissues from locations as far as 25 km away from the research bases [146]. PBDEs were also detected in marine sediments from and close to Winter Quarters Bay [146].

A large proportion of Antarctic biota live in, or in close proximity to, the marine sediments. These bottom dwelling organisms throughout Erebus Bay are therefore likely exposed to micropollutants via the sediments, and potentially at biologically relevant levels as observed in Whakaraupo Harbour. The biologically active micropollutants mParaben, pParaben, BP-3, E2 and EE2 were detected in the sediment dwelling clams. Animals feeding on these clams will therefore be exposed to estrogenic chemicals in the lower ng g^{-1} range (wet weight basis). Other sediment dwelling organisms such as polychaete worms which are the main food source for some Antarctic fish, may also accumulate these micropollutants. Predatory species such as seals feeding on contaminated fish may also become exposed to micropollutants. Dietary exposure of 7 mg kg^{-1} pParaben has been reported to induce vitellogenin production in fish (*Oncorhynchus mykiss*)[114]. Consumption of food containing 5 – 20 mg EE2 kg^{-1} produced a skewing of sex ratios in developing rainbow trout fry (*Oncorhynchus mykiss*) by 60 – 94% depending on exposure [276]. Another study reported vitellogenin production and delayed sexual maturation in male mosquito fish (*Gambusia affinis*) exposed to concentrations of EE2 and low as 1 μg EE2 g^{-1} food [277].

The bioaccumulation rates of steroid hormones in fish can be sensitive to the metabolic rates of the fish [274]. Antarctic biota generally have very slow metabolisms and are slow growing [278]. This may reduce the excretion rates of potentially harmful chemicals, therefore leading to longer *in vivo* exposure periods. Critical periods of biological development may therefore also be longer than in other aquatic organisms in different regions of the world. During this

time endocrine disruption may have a particularly severe detrimental effect. Antarctic biota may therefore be particularly sensitive to the effects of micropollutants.

4.4.2 Potential Effects on the Scott Base WWTP Biofilm

Wastewater treatment at Scott Base is facilitated by passing the wastewater through a series of biofilm beds housing the microbial communities of the WWTP. Acute exposure of these microbial communities to toxic chemicals may adversely affect microbial health and therefore the treatment efficiency of the WWTP, such as was observed in the Whakaraupo WWTP (Chapter 3, Section 3.3.4.1). The high concentrations of the detected micropollutants OP, 4-MBC, BP-1, and triclosan in the Scott Base effluents are a cause of concern because of their possible effects on the microbial community.

Maximum concentrations of OP, 4-MBC, BP-1, and triclosan reached 7 μg L^{-1}, 11.7 μg L^{-1}, 6.8 μg L^{-1}, and 0.8 μg L^{-1} respectively. These concentrations are near or above those at which adverse effects on microbiota have been observed. Adverse effects on the growth of the cyanobacteria *Microcystis aeruginosa* were observed at concentrations of OP as low as 5.6 μg L^{-1} [124]. In the green algae species *Desmodesmus suspicatus* toxic effects have occurred from exposure to the UV filters BP-3, 4-MBC, and OMC, with 72h-EC_{10} values ranging between 210 – 560 μg L^{-1} [109]. For the aquatic invertebrate *Acardia tonsa* the EC_{50} values for BP-1 ranged between 490 – 1,500 μg L^{-1} [109]. For triclosan, effects on algal growth have been observed at concentrations below 1 μg L^{-1} [1]. Continuous exposure of a biofilm community comprised of algae, protozoa, and micrometazoan species to 10 μg L^{-1} triclosan, which is a concentration relevant in wastewater influents [279], resulted in reduced algal biomass and a change in the bacterial community [279]. Other studies have also shown algae and its community structures to be highly sensitive towards triclosan [280, 281]. However, a wide variety of other aquatic organisms, including microorganisms and fish larvae are also sensitive towards triclosan toxicity [62]. Due to this toxicity whole ecosystems, both within and outside the WWTP can potentially be disturbed [62].

It is therefore possible that the fluctuating influent volumes and temperatures throughout the year may not be the only environmental factors which affect the treatment efficiency of Antarctic WWTPs. The high concentrations of certain micropollutants such as alkylphenols, UV filters, and triclosan may also adversely impact the treatment efficiency of Antarctic WWTPs.

4.5 Conclusions

This study is the first to report on the presence of a range of micropollutants in the WWTP sewage effluent of two Antarctic research stations and the receiving coastal environment.

During the 2009/2010 research season the Scott Base effluents contained OP, 4-MBC, BP-3, triclosan, BP-1, BPA, and E1, while the McMurdo effluents contained only BP-3, BP-1, and BPA. During the 2012/2013 research season the effluents of Scott Base contained mParaben, bParaben, OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, E1, EE2, and Cstanol. Detected concentrations were comparable to those in WWTP effluents worldwide. However the concentrations of OP, 4-MBC, BP-1, E1, and EE2 in some effluent samples during the 2012/2013 research season were higher than those previously reported internationally. These high analyte concentrations are postulated to impact the biofilm component of the WWTP of Scott Base, thereby adversely affecting the treatment efficiency of the plant. The concentrations of target analytes in the Scott Base WWTP during the 2012/2013 season did not show any significant temporal trends. The ozonation of the Scott Base sewage effluents may only have a limited impact on the concentrations of the target analytes.

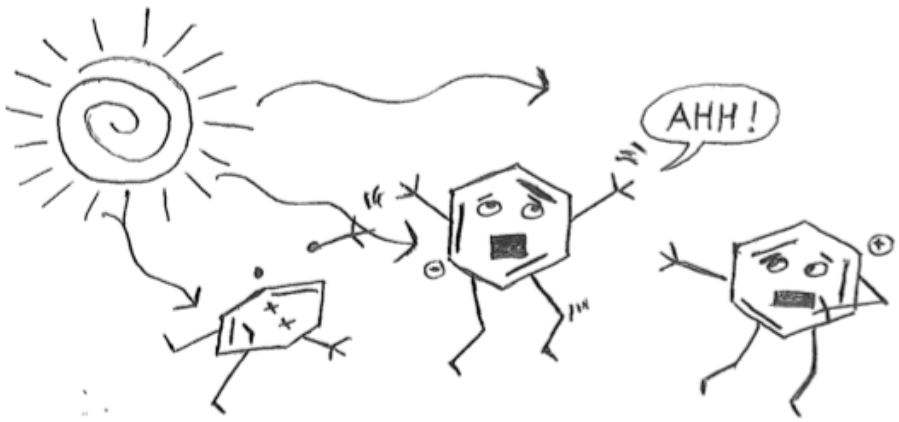
Target analytes were detected in the seawater during both research seasons. In 2009/2010 the detected target analytes were mParaben, pParaben, bParaben, OP, 4-MBC, BP-3, triclosan, methyl triclosan, BP-1, BPA, and OMC. In 2012/2013 detected target analytes were mParaben, pParaben, bParaben, OP, 4-MBC, BP-3, BPA, OMC, E1, EE2, and E3. The sea ice around Erebus Bay was found to be a sink for micropollutants as it contained OP, 4-MBC, BP-3, BPA, OMC, E1, and EE2 at concentrations comparable to those in the seawater. Target analytes concentrations in the seawaters were similar to international seawater data, and were lower in 2012/2013 compared to 2009/2010. During both research seasons target analytes were detected in all seawater samples, including those from the reference site at Cape Evans, located 25 km up-current from the identified point sources. Similarly to the Whakaraupo Harbour study the target analytes mParaben and OMC were frequently detected in the seawater but not the sewage effluents. The practice of tide-cracking has been identified as a possible explanation for these observations. The concentration data of detected target analytes in Erebus Bay seawater are highly comparable to the data obtained in the Whakaraupo Harbour study.

The target analytes mParaben, pParaben, OP, BP-3, E2, EE2, and Cstanol were found to bioaccumulate in marine biota. BP-3 was found to preferentially accumulate in clam tissues, while mParaben preferentially accumulated in fish muscle tissues. Bioaccumulation of mParaben in fish significantly correlated with fish fillet size. This is the first time paraben preservatives have been demonstrated to bioaccumulate in a field study. A preliminary assessment of the potential risks of the detected analytes shows that all detected target analytes have the potential to associate with sediments, which may provide a long-term sink of micropollutants. A larger than expected area around the research stations, and therefore a large number of animals within Erebus Bay, in particular sediment dwelling organisms, may

therefore be impacted by sewage discharges. Many aquatic species in Antarctica have slow metabolisms and are slow growing, which may enhance the risks these micropollutants pose to them.

CHAPTER FIVE

INFLUENCE OF TEMPERATURE AND LIGHT INTENSITY ON THE PHOTODEGRADATION RATES OF SELECTED MICROPOLLUTANTS



5 Influence of Temperature and Light Intensity on the Photodegradation of Rates of Selected Micropollutants

5.1 Introduction

The results of Chapter 3 and Chapter 4 indicate the ubiquitous presence of micropollutants in New Zealand and Antarctic coastal environments. Once in the environment micropollutants are subjected to a range of natural removal processes, including sorption to sludge and sediments, calcification, and microbial degradation [6]. Photochemical degradation, photolysis, or photodegradation, is a further potentially significant removal mechanism for many organic micropollutants [151]. However research into its significance is still in its early stages [151]. There is also limited data on photodegradation processes of organic micropollutants in polar environments. Some persistent micropollutants such as BPA and EE2, can remain in surface waters for days, weeks, and even months [282, 283], during which time they can potentially have a biological effect on the aquatic biota.

Previous studies have demonstrated that a range of hydrophilic and hydrophobic organic micropollutants, including pharmaceuticals [160], BPA [213], natural and synthetic steroid hormones (e.g. EE2) [214], NP [215], OP [194], triclosan [195], organic UV filters [216], phthalates [217, 218], and paraben preservatives [115] can undergo photodegradation. Experimentally determined half-lives can range from hours to several days [194, 195, 213, 215, 216, 284]. However these studies have investigated photodegradation under temperature and irradiance conditions that occur in mid-latitude, temperate climates. Polar conditions are characterised by extreme cold, semi-permanent sea ice cover, and radically fluctuating light conditions. Only a few studies have investigated the photolytic degradation of organic pollutants in seawaters [195], focusing instead on freshwater systems such as river and lakes [160, 194, 215]. The photodegradation behaviour of micropollutants should also be investigated in seawater matrices. The differences in salinity and dissolved organic matter (DOM) species [285] between seawater and freshwater may play a key role in regulating photodegradation processes. The photodegradation rate of triclosan has for example been shown to be enhanced in seawater compared to freshwater [195].

Photodegradation of organic contaminants has also been shown to occur within snow and ice [266], with both direct and indirect (Section 5.1.1) photodegradation mechanism observed. Photodegradation mechanisms of studied organic contaminants have been shown to be altered

by the ice matrix due to the changes in optical properties of the ice compared to water, and the altered substance-ice or substance-substance interactions that may occur in ice [266]. This has lead to the formation of reaction products from halogenated parent compounds that were different to those produced in liquid water, with some having toxic effects on organisms [266]. Further studies on the photochemical degradation mechanisms within ice are required, but are hindered by the difficulty in preparing adequate snow and ice mimics in controlled laboratory settings [266].

Light intensity and temperature can affect the photodegradation rates of organic contaminants. The photodegradation rates of triclosan and OP have been shown to decrease with decreasing irradiance [286, 287]. Similarly for OP decreasing temperatures were also shown to decrease the photodegradation rate [288]. However these studies did not systematically alter irradiance and temperature conditions, and were not conducted in seawater. Under polar conditions of reduced light and extreme cold micropollutants may persist for longer than in temperature climates. This may lead to Antarctic marine life being exposed to micropollutants at higher concentrations and for longer periods of time than would be the case in temperate regions. The current understanding of micropollutant fate and behavior is derived from investigations in temperate environments. This knowledge may have limited applicability when assessing the fate, behaviour, and impact of micropollutants under Antarctic climatic conditions. For example, modelled predictions on the half-life of triclosan in a lake at 60°N in Norway show an increase from 18 days in summer to up to 2,000 days in winter [116]. It is therefore important to investigate the photodegradation potential of micropollutants under Antarctic conditions as the influence of low temperatures and reduced sunshine on the photodegradation rates of micropollutants is unknown.

The overall aim of this study was to assess the likelihood of photodegradation occurring under Antarctic conditions. Six compounds were selected for further investigation, namely mParaben, BPA, EE2, BP-3, triclosan, and OP. These were chosen based on their detection frequency in Whakaraupo Harbour (Chapter 3) and Erebus Bay (Chapter 4), and on their environmental prevalence based on reported literature. With the exception of mParaben these micropollutants have been shown to photodegrade under temperate conditions [160, 195, 288-290].

The objectives of this study were to:

- investigate the photodegradation of mParaben, BPA, EE2, BP-3, triclosan, and OP in MQ water and seawater to allow for comparisons to be made with predominantly freshwater focused studies,

- investigate the photodegradation of mParaben, BPA, EE2, BP-3, triclosan, and OP over a range of irradiance and temperature levels in MQ water and seawater to determine if a simple predictive model can be built from this data as a proof of concept, and
- to predict how photodegradation rates for these chemicals may change under Antarctic climatic conditions.

5.1.1 Photodegradation of Organic Compounds

Photodegradation can be divided into two categories; direct and indirect [291]. For direct photolysis to occur the compound requires the presence of a system of delocalized π-electrons known as a chromophore [291], which has the ability to absorb photons. Benzene rings, double bonds, and any associated heteroatoms fulfil this requirement. The chromophore absorbs actinic radiation (between 290 – 800 nm depending on the chromophore), causing the compound to become unstable and subsequently degrade [292]. As the six selected micropollutants contain at least one benzene ring, there is the potential for direct photodegradation to occur.

Indirect photodegradation occurs via a chemical reaction of the compound of interest with a reactive chemical species generated by other light absorbing organic molecules, such as dissolved organic matter (DOM) [293]. These reactive chemical species include hydroxyl ($OH\bullet$) or superoxide radicals ($O_2^-\bullet$), as well as singlet oxygen ($^1O_2$) [293] and hydrogen [294]. This indirect pathway can degrade organic compounds that are not readily susceptible to direct photolysis [213]. Indirect photodegradation requires the presence of a photosensitizer in an excited triplet state, or the presence of short-lived radical species (e.g. from nitrate ions) or singlet oxygen species [293]. DOM is the most common source of triplet states and radicals, as it is ubiquitous in surface waters. DOM primarily absorbs light between 300 – 500 nm [293], generating excited triplet states, reactive oxygen species such as $OH\bullet$, peroxyl radicals ($ROO\bullet$), $^1O_2$, and non-oxygen containing radicals [213, 295]. These reactive species react with other molecules present in solution, thereby causing their degradation.

Naturally present aromatic and coloured organic matter tends to be very photosensitive, and are thought to activate, and therefore enhance, the degradation of organic pollutants which do not posses chromophores [213]. However, DOM has also been shown to decrease the rate of degradation of contaminants as it can absorb photons required for direct photolysis, without producing reactive species themselves [116]. Whether inhibition or enhancement occurs may depend on the season, as different light conditions, growth and decomposition phases of

plants, and changing weather patterns can alter the composition and physical mixing of DOM in surface waters. [293]

Modelling studies suggest that OH• radicals are the dominant reactive species in organic-poor waters, whereas $^1O_2$ is more dominant in organic-rich waters [296]. Another important source of radicals is H_2O_2, which can occur naturally in the environment, and readily produces OH• radicals under sunlight conditions. Algae have been shown to play an important role in the amount of H_2O_2 present in natural waters, with H_2O_2 degradation facilitated under dark conditions, and production facilitated under sunlight conditions [297]. Algae are also one of the most important sources of DOM in natural waters [298, 299].

Due to the wide variety of radicals that can form in aquatic systems there is the potential for a number of different indirect photodegradation pathways, and hence degradation products, to occur. The overall degradation rate (k) of any compound can be described as the sum of the rates of all degradation pathways that occur (3).

$$k_{overall} = k_{direct} + \Sigma k_{indirect} \qquad (3)$$

These degradation rates are assumed to follow first-order kinetics, and can be expressed using equation (4):

$$\frac{\delta(c)}{\delta(t)} = -kc \qquad (4)$$

where the change in concentration c over time t equals the rate k times concentration. Indirect photolysis can also be assumed to follow first order kinetics because DOM is present in excess amounts, such that any second order processes become pseudo-first-order [300]. This is a result of the DOM concentration changing very little over time as photodegradation occurs. This effectively removes the concentration dependence of DOM in any second-order process that is occurring. The integrated form of (4) is

$$c = c_0 \, e^{-kt} \qquad (5)$$

where c_0 is the starting concentration. The natural log form of (5) is (6).

$$\ln[c] = [c_0] - kt \qquad (6)$$

If the reaction in question follows first-order kinetics then a plot of the natural log of concentration against time will give a straight line, with the slope equal to the rate of the photodegradation process. The half-life of the compound can subsequently be calculated by substituting k into equation (7):

$$t_{1/2} = \frac{\ln(2)}{k} \qquad (7)$$

5.1.2 Environmental Conditions in Erebus Bay

5.1.2.1 Ocean Temperature

The ocean waters in Erebus Bay are among the coldest and iciest in the world [301]. This is due to its high latitude location and proximity to the Ross Ice Shelf, which is a source of cold melt water [301]. The ocean temperature remains at -1.9°C for a large part of the year (July – December) [302]. The temperature begins to rise slowly in December, reaching up to -0.35°C in late January [302]. Over January – March large fluctuations in temperature occur, with smaller fluctuations continuing until July [302].

5.1.2.2 Irradiance Conditions in Erebus Bay

Irradiance levels reaching the earth's surface each month in Erebus Bay, averaged over a 22-year period [162] are provided in Table 5.1. Irradiance levels under clear sky conditions (cloud cover <10%) are also provided, and are higher than the monthly averages. In Erebus Bay little or no sunshine reaches the earth's surface between April – September. Continuous 24-hour sunshine conditions begin in late October and end in mid-February [303]. In addition, levels of UV-B radiation (280 – 320 nm) increase during the summer season due to the hole in the ozone layer [304]. This may however be mitigated by the strong absorption of UV light by the sea ice [305]. Maximum irradiance conditions occur in December, with 735 W m^{-2} reaching the surface over this period, with up to 1010 W m^{-2} on a clear day.

Table 5.1: Average 22-year monthly solar irradiances and clear-sky solar irradiances (W m^{-2}) at 77°S 166°E (McMurdo Station & Scott Base) and at 43°S 172°E (Lyttelton, see Section 5.3.8.1) [162].

		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
McMurdo	Average	645	368	148	18	0	0	0	30	94	306	577	735
McMurdo	Clear sky	897	544	210	24	0	0	0	50	120	420	813	1010
Lyttelton	Average	581	504	399	276	183	143	161	233	343	451	554	580
Lyttelton	Clear sky	867	747	567	391	254	200	224	332	497	678	836	900

5.1.2.3 Sea Ice Conditions in Erebus Bay

Annual land-fast sea ice (ice attached to the coastline) can grow to a thickness of between 1.5 and 2 meters [306]. In Erebus Bay sea ice can be up to 2 m thick at the end of the ice growth season in December [265]. Snow covering the top of the ice ranges in depth from 0 – 60 cm, with an average of 15 cm [265]. However there are large areas which are snow free because of katabatic winds blowing off the continent [265]. These conditions were observed during the 2012/2013 research season field work (Chapter 4, Section 4.2.4.2). Measured sea ice

thickness ranged between 158 – 229 cm. Snow depth ranged between 0 – 60 cm. Large areas of the upper half of Erebus Bay were found to be snow-free, with higher snow cover found close to the research stations.

Sea ice conditions can vary considerably from year to year. In Erebus Bay, sea ice generally begins to form around late April/early May, and can begin to break up from early December through to early February [243]. Bottom melting of the sea ice begins in mid-December, and progresses rapidly until breakout [307]. Sea ice also melts internally. As the molten brine drains from the sea ice the ice becomes more turbid [265]. The growth rate and ultimate thickness of the sea ice largely depends on snow cover and proximity to the coast or the ice shelf [307].

The presence of the B-15 iceberg, which calved off the Ross Ice Shelf in March 2000 [308] drastically changed the sea ice dynamics until 2011, retaining the sea ice within Erebus Bay for longer during each season [243], and strongly affecting algae growth and other wildlife [308]. The multi-year sea ice subsequently began to accumulate to an average thickness of 221 cm [263]. The sea ice directly off Scott Base and McMurdo station was observed to be over three meters during the 2009/2010 research season field work for this thesis. Annual reports until the 2010/2011 season produced by the National/Naval Ice Centre state the annual sea ice was retained around Ross Island as far north as Cape Royds, implying that the entire coastal areas off McMurdo station and Scott Base were continuously covered by sea ice for almost 13 years [263]. Staff stationed at McMurdo Station and Scott Base reported the sea ice breaking off the coast in mid-February 2011 following a severe weather event [264].

5.1.2.4 Effect of Sea Ice on Irradiance

Sea ice along the coast does not completely break away for large parts of the summer season, and can therefore provide protection from UV radiation [309]. However, sunlight does still penetrate the sea ice surface, as is evident in the growth of ice algae underneath the ice surface [310, 311]. Experimentally measured under-ice irradiance levels have been determined to be less than 1% of that measured at the surface [312-314]. Sea ice thickness decreases throughout the Antarctic summer from bottom melting, until the ice breaks away [307]. During this period irradiance levels also increase as summer progresses [315]. These processes occur in parallel, with the result that increasing amounts of light can penetrate the water column, until the ice eventually breaks away. Photodegradation processes may therefore become a significant removal mechanism for organic micropollutants within Antarctic seawater some time before the ice breaks away.

This reduction in irradiance will reduce the photochemical degradation potential of organic micropollutants in seawater covered by sea ice. The intensity of light *I* which passes through a substance is related to the initial intensity I_0 of light according to the inverse exponential power law (also known as the Beer-Lambert Law) (8),

$$I = I_0 \, e^{-\alpha x} \qquad (8)$$

where *x* denotes the path length of light in meters through the material, and α (m^{-1}) is the attenuation coefficient of the material. Because light intensity is directly proportional to radiant energy density (irradiance), irradiance can be used in this equation instead of intensity. From (8) it can be seen the larger α becomes the less light can pass through the material. Pure ice exhibits strong absorption in the UV spectrum (λ < 170 nm), and becomes very weak in the visible, with a minimum near 400 nm [305]. Absorption begins to increase again in the near infrared (1 – 3 μm), becoming very strong in the infrared (3 – 150 μm), before decreasing again in the microwave region (λ < 1 cm) [305]. The absorption spectrum of water is similar to that of ice from the UV in to the middle IR spectrum [305].

The spectral properties of ice are strongly affected by snow cover, and by the structural properties of the ice, because crystal defects and impurities can cause scattering of light [316]. Impurities include salt, gas bubbles, soot, sediments, algae, brine cells and capillaries, and micropores left behind after the brine cells and capillaries have drained [312, 316, 317]. These attenuation sources add up so that under-ice irradiance is typically less than 1% than that of the surface [312, 313]. Moreover, the spectral composition shifts towards the blue-green spectrum (450 – 550 nm) as it passes through the sea ice [312, 318]. As such, sea ice can attenuate a significant proportion of light compared to pure ice.

Light transmission measurements were performed on multi-year sea ice at Cape Armitage (between McMurdo Station and Scott Base) on two separate occasions (2002 and 2003, Figure 5.1) [314].

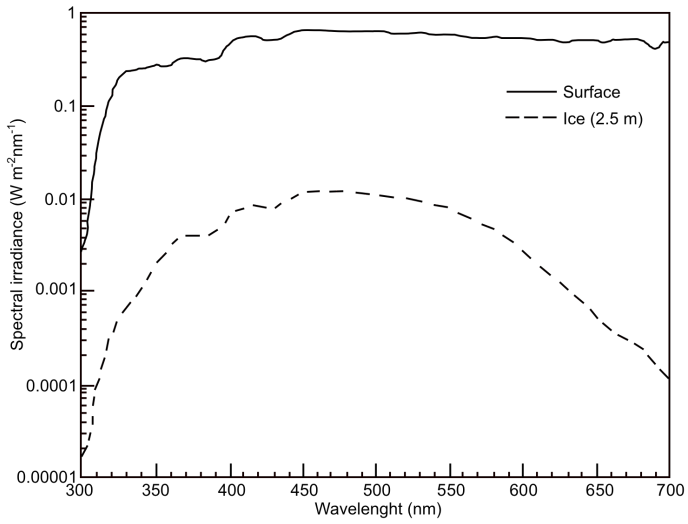


Figure 5.1: Light transmission measurements between 300 – 700 nm on the surface and beneath 2.5 m of multi-year sea ice at Cape Armitage from 2002, reproduced from Lesser et al [314].

Applying equation (8) to these measurements a sea ice attenuation coefficient α of 1.787 m^{-1} and 1.551 m^{-1} for 2002 (2.5 m ice thickness) and 2003 (3.1 m ice thickness) respectively was calculated. This corresponds to an attenuation of 98.9% and 99.2% respectively. Similarly, this approach can be applied to the water column beneath the ice surface. Using the measurements from the same study, a water attenuation coefficient of 0.165 m^{-1} and 0.131 m^{-1} for 2002 and 2003 respectively was calculated. The average attenuation coefficients are 1.669 m^{-1} for sea ice, and 0.148 m^{-1} for ocean water. Using these values, it is predicted that 1.38 m of sea ice, or 15.56 m of open ocean water, is required to reduce the irradiance level to 10% of its original intensity. These values assume there is no snow cover on top of the sea ice. Snow can decrease the amount of light that can penetrate into the water column, and hence further limit photodegradation processes However, in the Erebus Bay large areas of sea ice do become snow free where katabatic winds have blown away the snow cover [265]. The presence of sea ice will therefore protect micropollutants in the seawater from photodegradation.

5.2 Methods

The experimental methods used for the photodegradation experiments are presented in Chapter 2. Working solutions of the selected analytes in MQ and seawater were exposed to a range of irradiance and temperature conditions in triplicate between 330 – 650 W m^{-2} and 7 – 27 °C (monitored with a radiometer and HOBO temperature logger) over a period of seven hours, for a total of twelve experiments. Samples taken at regular intervals were analysed by HPLC with UV-DAD detection for the quantification of analyte concentrations in solutions. Photodegradation rates were calculated from the measured concentration of analytes.

5.3 Results and Discussion

Only triclosan and OP showed significant photodegradation, with up to 100% for both analytes. Photodegradation of up to ~20% (depending on experimental parameters) was observed for BPA, EE2, and BP-3. However the degradation curves exhibited poor regression fits, and the calculated half lives were highly variable with up to a five-fold difference between the three replicates. Lastly, mParaben remained stable over the experimental period with no degradation occurring. Due to the limited degradation of mParaben, BPA, EE2, and BP-3 only limited conclusions could be drawn from the data. The photochemical degradation of triclosan and OP will therefore be the main focus of this chapter.

5.3.1 QA/QC

Dark controls of the MQ and seawater solutions remained stable over the experimental period. The working solutions stored at 4°C also showed no signs of degradation during their use in the twelve experiments. Blank controls showed minor signs of baseline variability at 228 nm, but did not interfere with sample analysis.

5.3.2 Data Analysis

Rate constants (k) were determined from concentration (c) and time (t) data by least-squares regressions fitted to the linearised first-order rate equation (6) in Microsoft Excel (2008 for Mac, Version 12.1.0).

$$\ln[c] = [c_0] - kt \qquad (6)$$

Half lives were calculated from the degradation rate constants k using equation (7).

$$t_{1/2} = \frac{\ln(2)}{k} \qquad (7)$$

The HPLC data were compiled and the half-lives calculated using Excel prior to the statistical analyses in R. The complete non-averaged triplicate data were used in the analyses. The irradiance and temperature data obtained from the radiometer and temperature logger measurements were averaged over the seven hour experimental period and used for the data analysis instead of the nominally defined irradiance and temperature settings. Differences in photodegradation rates between MQ water and seawater were tested with a Welch Two Sample t-test. Correlations of the effects of irradiance and/or temperature on the degradation rate of the target analytes were calculated in R (Version 2.14.1 for Mac) using a multi-linear regression model based on the following mathematical principles.

The photodegradation rate of any chemical can be directly related to irradiance exposure. The experimentally measured wavelength dependant photodegradation rate $k(\lambda)$ can be expressed using equation (8) [92],

$$k(\lambda) = 2.3\ W(\lambda)\ \frac{A}{V}\ \varepsilon(\lambda)\ l(\lambda)\ \Phi(\lambda) \qquad (8)$$

where

$W(\lambda)$ = the intensity of the incident radiation expressed as spectral photon fluence, $W(\lambda)$ (number of moles of photons per square centimeter per second),

$\Phi(\lambda)$ = the reaction quantum yield at each wavelength (in moles of reactant degraded per mole of photons),

A = total irradiated area (cm^2),

V = volume of sample cell (L),

$\varepsilon(\lambda)$ = molar absorptivity of the sample medium at each wavelength (L mol^{-1} cm^{-1}), and

l = path length of the sample cell at each wavelength.

Alternatively, the energy input $W(\lambda)$ may be expressed in terms of irradiance ($I(\lambda)$ in W m^{-2}) rather than photon fluence, by measuring or calculating the total energy of the photons arriving at the surface of the sample rather than simply the number of photons. The corresponding reaction yield at each wavelength, given as $Q(\lambda)$ is expressed in terms of the number of moles of reactant photodegraded by per unit light energy input (moles per Joule), using equation (9).

$$k(\lambda) = 2.3\ I(\lambda)\ \frac{A}{V}\ \varepsilon(\lambda)\ l(\lambda)\ Q(\lambda) \qquad (9)$$

In the context of environmental chemistry, only the integrated rate constant across the solar radiation spectrum is of practical interest. To obtain this integrated form of equation (9) the path length and molar absorptivity can be generally assumed to be wavelength-independent. However, while the quantum yield $\Phi(\lambda)$ in equation (8) is generally assumed to be wavelength independent [92] this may not be the case for compounds which absorb light over a broad wavelength range exhibiting several maxima of light absorption [92]. Similarly, the reaction yield $Q(\lambda)$ may therefore also not be wavelength independent under some circumstances. In an environmental photodegradation context $Q(\lambda)$ is expected to be

approximately constant, except potentially at small wavelengths as explained below, and would have an only minor impact on the measured results.

Sunlight below ~300 nm is effectively filtered out by the atmosphere, and a light filter was used in all photodegradation experiments of this study to remove light below ~300 nm. Furthermore, organic micropollutants such as those investigated in this study absorb only small amounts of light above 300 nm (e.g. triclosan, Figure 5.2). Therefore there is only minimal overlap between the absorption spectrum of the analyte and the spectrum of the radiation source. It is photons with wavelengths from this overlap that are likely to most heavily influence the photodegradation rate of the particular compound. This range of wavelengths is the region where the reaction yield is most likely dependent on wavelength (Figure 5.3). However, due to the limited number of photons present at these wavelengths the shape of the overall product of irradiance and the reaction yield curves (I(λ) x Q(λ), Figure 5.3) remains, for all intense and purposes, independent of wavelength.

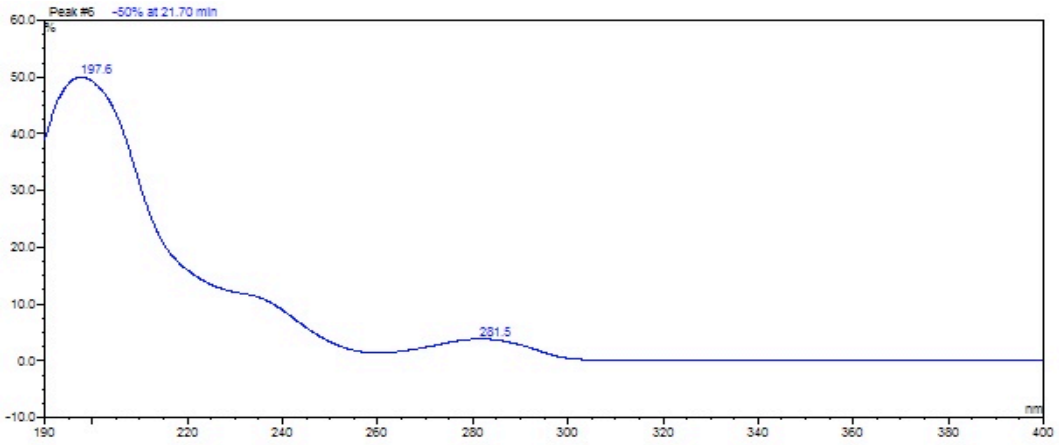


Figure 5.2: UV spectrum of triclosan. Minor absorption occurs above 300 nm.

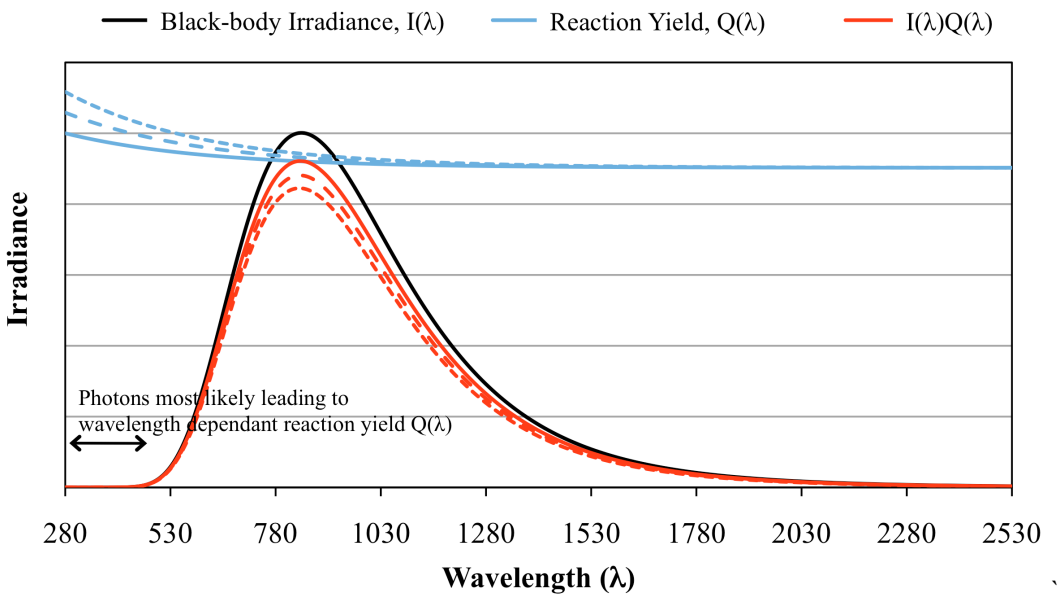


Figure 5.3: Illustration of a black-body radiation (black line), the potential wavelength-dependent reaction yield Q(λ) (blue lines) and the resulting pseudo-wavelength independent product of I(λ) and Q(λ) (red lines). Arrow indicates region of high energy photons which will most likely affect the overall photodegradation rate. Note the only small changes in I(λ)Q(λ) as the reaction yield wavelength dependence is increased (dashed lines).

An approximately wavelength independent quantity, the normalized reaction quotient (in moles per Joule of incident light energy) can therefore be defined with equation (10),

$$q = \frac{\int I(\lambda)\, Q(\lambda)\, d\lambda}{\int I(\lambda)\, d\lambda} \qquad (10)$$

which gives the following equation (11) for the relationship between photodegradation rate constant and total (integrated) irradiance *I*.

$$k = 2.3\, I\, \frac{A}{V}\, \varepsilon\, l\, q \qquad (11)$$

Irradiated area (*A*), sample volume (*V*) and path length (*l*) are prescribed by the experimental setup, the molar absorptivity (ε) may be easily measured or estimated from literature values, leaving q as a constant of proportionality relating k to I that may be determined from a series of experiments measuring the variation of k with I. A plot of the experimentally determined photodegradation rates k against irradiance will therefore result in a straight line.

The temperature dependant changes on degradation rates on the other hand can be readily determined using the Arrhenius equation (12).

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \qquad (12)$$

A plot of ln(k) against the inverse of temperature in Kelvin will therefore give a straight line. Alternatively a plot of k against $e^{1/T}$ will also give a straight line. In this way a multi-linear regression model can be calculated using the linear relationships of k against irradiance and $e^{1/T}$ to simultaneously model the effects of irradiance and temperature on the photodegradation of the target analytes.

5.3.3 Photodegradation of Triclosan

Triclosan was photodegraded to below the HPLC limits of detection over the seven-hour exposure in both MQ and seawater in all experiments. Half-lives ranged from 0.9 – 4.7 hours in MQ, and 0.2 – 1.1 hours in seawater (Table 5.2). An experimentally obtained exponential degradation curve for triclosan is shown in Figure 5.4a. Degradation occurred via first order kinetics as shown in Figure 5.4b. The three replicate half-lives (hours) calculated at each set of environmental conditions are presented in Table 5.2. The variability between the triplicates differed between each experiment, with %RSDs ranging between 13% – 52% in MQ water and between 7% – 48% in seawater.

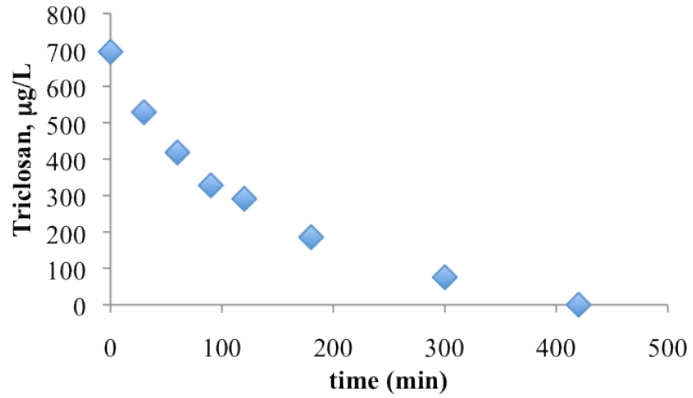


Figure 5.4a: Exponential decay curve of triclosan in MQ water at 330 W m^{-2} and 14 °C.

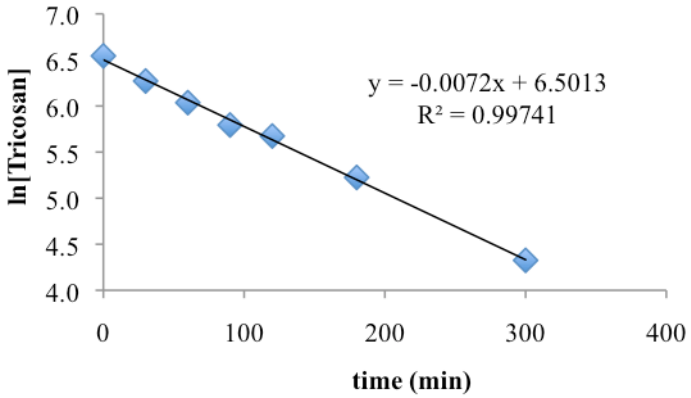


Figure 5.4b: Linearised plot of Figure 5.4a, confirming the first-order degradation of triclosan.

Table 5.2: Experimentally measured half-lives (hours) of triclosan in MQ and seawater.

	MQ Water			Seawater		
	330 W m^{-2}	500 W m^{-2}	650 W m^{-2}	330 W m^{-2}	500 W m^{-2}	650 W m^{-2}
7°C	2.2	1.7	3.2	0.7	0.4	0.6
	3.6	1.3	1.9	1.1	0.5	0.2
	3.3	2.0	1.5	0.7	0.5	0.5
14°C	4.6	1.6	1.6	0.8	0.4	0.3
	2.0	2.1	1.2	0.5	0.5	0.2
	2.0	1.9	0.9	0.6	0.5	0.2
21°C	3.0	1.6	2.0	0.5	0.4	0.3
	2.2	2.9	1.7	0.9	0.4	0.2
	3.1	2.1	0.9	0.4	0.5	0.3
27°C	4.7	1.7	1.8	0.9	0.4	0.5
	3.1	2.5	1.2	0.5	0.5	0.4
	2.5	2.2	1.1	0.7	0.4	0.5

The range of experimentally measured photodegradation rates and half-lives of triclosan are consistent with the range observed in the literature in MQ water and freshwater (Table 5.3). A previously reported half-life of 96 hours was reported in seawater [195]. These experiments were however conducted using a fluorescence lamp instead of a xenon arch lamp [195], possibly accounting for this large difference in half-lives. The photodegradation of triclosan was significantly enhanced in the seawater compared to MQ water (p = 6.6 x 10^{-11}, Welch Two Sample t-test). This enhancement is discussed in more detail in Section 5.3.7.

Table 5.3: Experimental and literature values of photodegradation half-lives (hours) of triclosan.

Matrix	Rate (min^{-1})	Half life (h)	Reference
MQ water	0.012 – 2.46 x 10^{-3}	0.9 – 4.7	This study
Seawater	0.069 – 0.010	0.2 – 1.1	
MQ water	1.68x10^{-2}	0.69	[319]
Fresh water	4.7 x10^{-2} – 2.6x10^{-2} (lake)	0.2 – 0.4	[116]
	0.155 (lake)	0.07	[320]
	2.08x10^{-4} (lake)	55.5	[63]
	0.25x10^{-2} (lake)	0.9	[63]
	6.02 x10^{-5} (lake)	192	[195]
	2.31 x10^{-3} (river)	5	[321]
Seawater	1.22 x10^{-4}	96	[195]

5.3.4 Photodegradation of OP

OP was photodegraded to below the HPLC limits of detection over the seven hour exposure in both MQ and seawater in all experiments. Half-lives ranged from 1.1 – 5.3 hours in MQ water, and from 1.4 – 4.5 hours in seawater (Table 5.4). An experimentally obtained exponential degradation curve for OP is shown in Figure 5.5a. Degradation occurred via first order kinetics as shown in Figure 5.5b. The three half-lives (hours) calculated at each set of environmental conditions for OP are presented in Table 5.4. The variability between the

triplicates differed between each experiment, with %RSDs ranging between 7% – 27% in MQ water and between 2% – 37% in seawater.

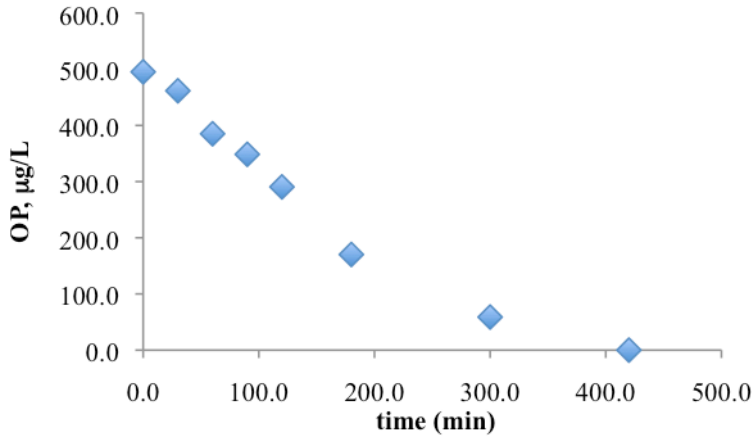


Figure 5.5a: Exponential decay curve of OP in seawater at 330 W m^{-2} at 27°C.

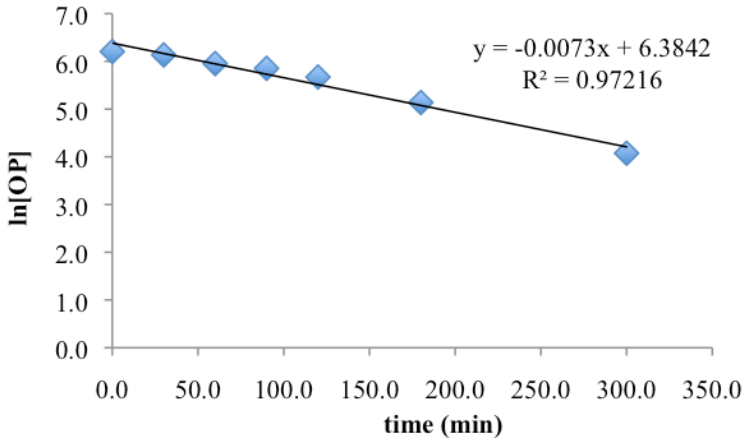


Figure 5.5b: Linearised plot of Figure 5.5a, confirming the first-order degradation of OP.

Table 5.4: Experimentally measured half-lives (hours) of OP in MQ and seawater.

	MQ Water			Seawater		
	330 W m^{-2}	500 W m^{-2}	650 W m^{-2}	330 W m^{-2}	500 W m^{-2}	650 W m^{-2}
7°C	3.3	3.9	4.0	2.3	3.1	3.9
	5.3	3.1	4.2	2.2	2.1	2.9
	4.3	4.3	4.6	3.4	2.5	3.2
14°C	3.3	2.2	2.4	2.2	2.2	1.4
	2.9	3.2	2.0	2.8	2.5	2.4
	4.8	2.9	3.2	2.4	2.1	2.2
21°C	4.2	1.6	1.9	2.5	1.7	1.5
	3.7	2.1	1.3	2.5	1.7	1.3
	4.6	1.8	1.4	4.5	1.8	1.6
27°C	3.6	1.2	1.5	2.1	1.6	1.6
	3.0	1.5	1.6	1.5	1.5	1.4
	3.6	1.6	1.1	1.6	1.6	1.4

The range of experimentally measured degradation rates and half-lives of OP are consistent with the range observed in the literature for MQ water and freshwater (Table 5.5). The photodegradation of OP was not significantly enhanced in the seawater compared to MQ water (p = 0.0780, Welch Two Sample t-test), and is explained in more detail in Section 5.3.7.

Table 5.5: Experimental and literature values of photodegradation half-lives (hours) of OP.

Matrix	Rate (min^{-1})	Half life (h)	Reference
MQ water	$0.010 – 2.18 \times 10^{-3}$	1.1 – 5.3	This study
Seawater	$8.46 \times 10^{-3} – 2.58 \times 10^{-3}$	1.4 – 4.5	
MQ water	5.4×10^{-3}	2.1	[221]
	0.28×10^{-3}	40.8	[288]
	$3.15 \times 10^{-3} – 5.33 \times 10^{-3}$	0.2 – 0.4	[287]
Freshwater	0.282×10^{-3} (lake)	41	[288]
	0.304×10^{-3} (river)	38	[288]
	$4.81 \times 10^{-3} – 1.92 \times 10^{-4}$ (tropical)	14.4 – 60	[194]
	$7.70 \times 10^{-4} – 5.78 \times 10^{-4}$ (lake, nonylphenol)	15 – 20	[215]

5.3.5 Photodegradation of mParaben BPA, EE2, and BP-3

5.3.5.1 mParaben

mParaben was the most photo-stable of the tested compounds. mParaben showed no signs of degradation under any experimental conditions. To date only limited data exists on the photodegradation of paraben preservatives. Only the TiO_2 mediated (2.5 g L^{-1}) photodegradation of mParaben has been shown to result in 80% mineralization after 6 hours irradiation time [322]. The photostability of paraben preservatives has been previously observed for paraben compounds closely related to mParaben. Under natural sunlight conditions *n*-bParaben and *t*-bParaben were shown to be stable, with half-lives of 350 – 410 hours and 350 – 580 hours respectively [323]. A second study on bParaben however observed fast photodegradation [115, 324], with up to 99% degradation within 1.5 hours of irradiation time at 254 nm [115]. Only wavelengths above 300 nm are however important for this current study. Benzyl paraben (BzParaben) also readily photodegraded, with a half-life of 11 – 15 hours [323].

5.3.5.2 BPA

A maximum of ~20% of photodegradation of BPA was observed over the seven hour exposure period. Due to this minimal degradation the measured degradations curves were irregular and did not directly fit an exponential decay curve. Half-lives therefore could not be calculated. The photostability of BPA has been observed in previous studies, with calculated half-lives of 235 hours in MQ and 17.4 hours in environmental waters [213].

5.3.5.3 EE2

A maximum of ~20% photodegradation was also observed for EE2 over the seven hour exposure period. Similar to the degradation of BPA the degradations curves for EE2 were irregular and did not directly fit an exponential decay curve Degradation of EE2 in MQ and seawater has previously been reported in the literature [325, 326]. The calculated half-lives were as high as 36 hours [326] and 126 hours [219] in river waters. Other studies have reported shorter half-lives of 28.4 hours [160] and 1.13 hours [327] in MQ water, 2.3 hours in river water [160], and 0.95 – 1.11 hours in river and seawater [327].

5.3.5.4 BP-3

The photodegradation of BP-3 was up to ~20% over the seven hour exposure period. As for BPA and EE2 the degradations curves were irregular and did not directly fit an exponential decay curve. Little to no degradation of BP-3 has been observed previously [328-330], even after irradiation periods of up to 100 hours [216]. In comparison Serpone *et al* [220] reported degradation of up to 20% in MQ water after an exposure of 2 hours.

5.3.6 Effect of Irradiance and Temperature on Photodegradation

5.3.6.1 Triclosan

Degradation of triclosan increased with increasing irradiance (Figure 5.6). Degradation rates in seawater were enhanced compared to MQ water.

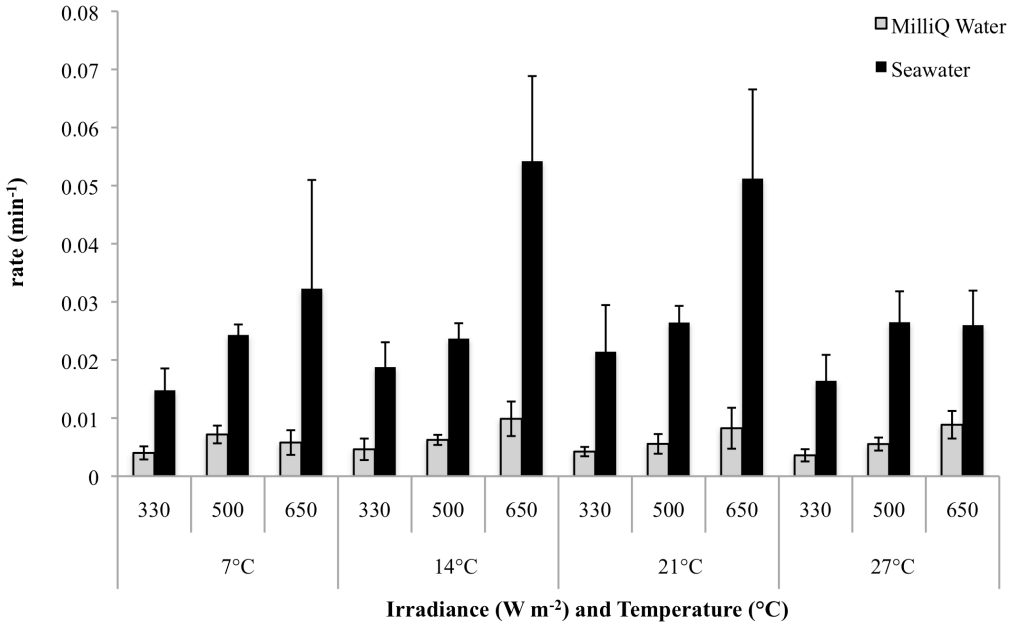


Figure 5.6: Average (± standard deviation, n=3) degradation rates (min^{-1}) of triclosan in MQ water and seawater from the twelve environmental condition settings.

Fitting the experimental data to the multi-linear regression model with the degradation rate (min^{-1}) as the dependent variable and I and $e^{1/T}$ as the independent variables (derived from equations (11) and (12)) showed that the photodegradation rate of triclosan was significantly correlated with irradiance in MQ water (p = 1.7 x 10^{-5}) and seawater (p = 3.5 x 10^{-5}). Temperature did not affect the photodegradation rate of triclosan in either MQ water (p = 0.932) or seawater (p = 0.879). Irradiance and temperature were also tested for covariance but did not interact with each other.

Previously published laboratory studies on triclosan have also reported decreasing degradation rates with decreasing irradiance [286]. Field studies have reported similar observations. Decreased triclosan degradation was observed at low water depths of a lake (95% reduction at 50 cm below the surface) [116]. Large seasonal changes in triclosan concentrations in surface waters due to the seasonal changes of sunlight intensity have also been observed [63]. Temperature independence suggests direct photolysis is the major degradation pathway, as this only involves the absorption of photons, which does not depend on the kinetic energy of the aqueous system. Previous studies have identified direct photolysis as the likely major degradation mechanism for triclosan [63, 116, 321]. The species most prone to photodegradation is thought to be the singlet excited state of triclosan [321]. Reported main degradation products are dichlorophenol [286, 320, 321, 331], chlorophenol [286, 320], phenol [286, 320], and dioxins [286] [195, 320, 321]. Most of these degradation products are produced by the cleavage of the ether bond. The main degradation mechanism is therefore thought to include this bond cleavage. Indirect photodegradation pathways for triclosan are thought to play only a minimal role [321].

5.3.6.2 OP

The degradation of OP increased with increasing irradiance and increasing temperature (Figure 5.7). Application of the same multi-linear regression model to the 4-*t*-OP experimental data as for triclosan showed the photodegradation rate of OP was significantly correlated with irradiance in MQ water (p = 2.3 x 10^{-5}) and seawater (p = 8.8 x 10^{-4}), and with $e^{1/T}$ in both MQ water (p = 4.1 x 10^{-6}) and seawater (p = 3.1 x 10^{-5}). Degradation rates were not enhanced in seawater compared to MQ water. Irradiance and temperature were also tested for covariance but did not interact with each other.

Only one study could be found on the effects of irradiance on OP degradation. This study also reported decreased degradation at decreased irradiance [287]. Decreased degradation at decreasing water column depths (analogous to decreasing irradiances) have also been reported for nonylphenol [215], a closely related compound. Decreased degradation of OP with decreasing temperature has also been reported in previous studies. OP photodegradation

increased from 14% of initial concentration after 8 hours irradiation at 15°C to 30% at 25°C [288]. The photodegradation rate of NP was similarly enhanced by increasing temperature, with degradation over 10 hours, increasing from 11% at 10°C to 41% at 25°C [332]. The TiO_2 assisted photodegradation of OP was also found to increase over the experimental temperature range of 30°C to 60°C [221]. The temperature dependence of TiO_2 assisted photodegradation has been observed for a wide range of other organic compounds, including phenol, oxalic acid, and the dye methylene blue [333].

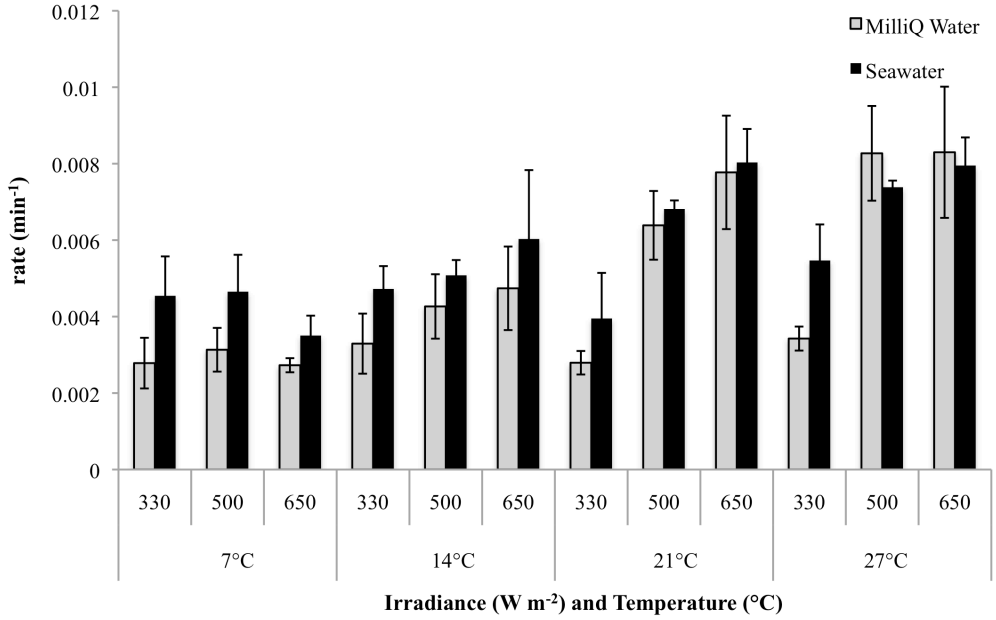


Figure 5.7: Average (± standard deviation, n=3) degradation rates (min^{-1}) of OP in MQ water and seawater from the twelve environmental condition settings.

A combination of direct and indirect photodegradation pathways have been proposed for OP. The main degradation mechanism of OP proposed by Mazellier [334] and Huang [335] involves the production of an OP• radical on the phenol ring through direct photolysis, which subsequently reacts with dissolved oxygen to form 4-*t*-octylcatechol. According to this mechanism the photodegradation of OP greatly depends on the presence of oxygen. This mechanism was confirmed by its enhanced degradation in oxygen-saturated water compared with argon-flushed [334] or nitrogen-flushed [335] water, with decreased generation of 4-*t*-octylcatechol observed in the nitrogen-saturated water [335]. Continuous bubbling of oxygen through the water further increased OP degradation compared to the oxygen-saturated water [334]. The formed OP radical was also observed to dimerise under high initial OP concentrations of ~ 9 mg L^{-1} [335], but which is approximately 15 times higher than the initial OP concentrations used in the present study. Reported photoproducts of OP are 4-*t*-octylcatechol [287, 334], phenol [288], 1,4-dihydroxybenzene [288], and 1,4-benzoquinone [288].

Using the Arrhenius equation (12) the activation energies for the degradation of OP can be calculated at each of the three experimental irradiance settings from the slopes of ln(k) against 1/T (Figure 5.8). The data and activation energies obtained in this way are summarized in Table 5.6. The activation energies ranged between 21.1 – 44.7 kJ mol^{-1}. At the 330 W m^{-2} irradiance setting the temperature dependent photodegradation of OP in MQ water and seawater was not as pronounced as at 650 W m^{-2} and 500 W m^{-2}. Activation energies in MQ water and seawater could therefore not be calculated at 330 W m^{-2}. A Japanese study has also conducted OP degradation experiments at various temperatures, and has reported an Arrhenius graph similar to Figure 5.8 [221]. However a TiO_2 catalyst was used to enhance the photodegradation of OP, and an activation energy of 18.6 kJ mol^{-1} was reported [221]. This falls into the same magnitude calculated in this study. However the Japanese activation energy would be expected to be lower than those reported in this study since a catalyst reduces the activation energy of a given reaction.

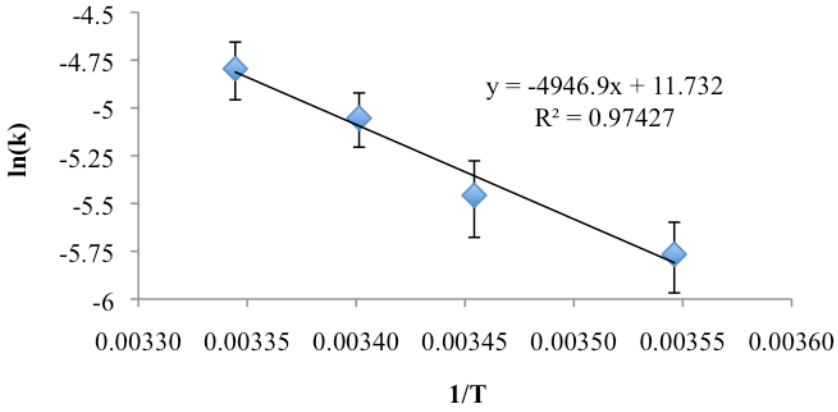


Figure 5.8: Arrhenius plot of averaged ln(k) (± standard deviation, n=3) against inverse temperature (Kelvin) of the degradation rates of OP at 7°C, 14°C, 21°C, and 27°C at 500 W m^{-2} in MQ water.

Table 5.6: Activation energies E_a of the temperature dependent degradation of OP, as determined from the slope of the Arrhenius plots.

	MQ water			Seawater		
Irradiance (W m^{-2})	Slope (10^3 K)	R^2	E_a (kJ mol^{-1})	Slope (10^3 K)	R^2	E_a (kJ mol^{-1})
650	-5.374	0.9409	-44.7	-3.950	0.8708	-32.8
500	-4.969	0.9730	-41.3	-2.542	0.9058	-21.1
330	-0.641	0.3565	*	-0.698	0.7113	*

*Data at 330 W m^{-2} was too variable to allow for a regression fit of the data.

5.3.7 Effects of Seawater on Photodegradation

Triclosan degradation in seawater was significantly enhanced compared to the MQ water (p = 6.6 x 10^{-11}, Welch Two Sample t-test). The photodegradation in the seawater increased between 3 – 4 fold. Literature data on the photodegradation behaviour of triclosan in different water types is contradictory. Some studies observed enhanced degradation in fresh and

seawaters compared to pure water [195], however most studies have observed the opposite [63, 116, 321], with degradation rates decreasing by up to 20% in lake water [116]. The cause for this decrease was identified as the filtering of light and the potential of organic matter to regulate pH [63, 116, 321]. However, DOM has experimentally been found to also be able to enhance the degradation of organic compounds with similar structures to triclosan, such as polychlorinated biphenyls (PCBs), at low DOM levels of up to 0.18 mg L^{-1} [294]. At higher concentrations the light filtering effect became more dominant and the photodegradation of PCBs was reduced [294]. As discussed in Section 5.3.6.1 the main degradation pathway of triclosan is thought to occur via a direct photolysis mechanisms. DOM is therefore expected to not play a major role in the photodegradation of triclosan.

The pH can also play a significant role on the photodegradation of triclosan. The anionic form of triclosan (pK_a = 8.1) can more readily absorb light than the molecular form [95]. The ionised form has been shown to degrade 19 times faster than the molecular form [116]. Other studies have also observed pH to be an influencing factor on triclosan degradation [63]. In this study the pH of the MQ water and seawater were ~5 and ~7.5 respectively. At pH = 7.5 ~20% of total triclosan is in the ionized form [95]. The ionised form of triclosan would therefore play an important role in the enhanced degradation observed in the seawater by this study. If approximately one fifth of the total triclosan is present in the ionized form, which degrades approximately 19 times faster than the unionized form [116], a four-fold increase in the photodegradation rate could be expected, as was observed in this study.

The photodegradation of OP was not enhanced in the seawater (p = 0.0780, Welch Two Sample t-test). As discussed in Section 5.3.6.2 the main photodegradation mechanism of OP is thought to involve dissolve O_2, thereby limiting the influence of DOM on its photodegradation rate. Other studies have, as was the case for triclosan, observed a reduction in its degradation in natural waters compared to pure water [194, 334]. This reduction was speculated to arise from the radical quenching properties of DOM, even though DOM can also be a significant source of radical species [194, 213, 295]. DOM such as humic acids are also postulated to attenuate the incident irradiation and reduce OP degradation rates [287]. However, enhanced instead of reduced degradation has also been reported in natural waters for OP [288] as well as nonylphenol [215]. Nitrates and Fe^{3+} have been shown to enhance the photodegradation of OP and the closely related compound NP due to their capacity to produce OH• radicals through photolytic processes [332, 335]. The presence of sulfates did not affect the photodegradation of OP [335]. Bicarbonate on the other hand was shown to decrease the photodegradation of OP and NP due to its capacity to increase the pH [288, 332, 335]. The photodegradation of OP is enhanced at high pH, similarly to triclosan, as deprotonated phenol groups such as those in OP show a greater photodegradation potential than the protonated

phenol group [335]. However the pK_a of OP is 10.33 [335]. At an environmentally relevant pH such as in the Adelaide seawater (pH ~ 7.5) only ~0.2% of OP is present in the deprotonated form. The enhanced photodegradation of deprotonated phenols may therefore have only limited relevance under the environmental conditions tested in this study.

5.3.8 Extrapolation to Antarctic Conditions

The multi-linear regression model used in Section 5.3.6 to test for significant changes in photodegradation rate with irradiance and temperature was extended to predict the photodegradation rates of triclosan and OP in seawater at reduced irradiance and temperature levels. Irradiance levels in Antarctica exceed 330 Wm^{-2} for only a brief period of the year, during the summer season (Table 5.1). It is therefore important to understand what photodegradation rates may be during the spring and autumn months when irradiance levels are below 330 W m^{-2}. While the model agreed well with the majority of the experimentally obtained data, the increasing data variability observed at decreased experimental environmental conditions made predictions at environmentally relevant low temperature and irradiance conditions too uncertain.

Photodegradation of triclosan and OP decreased with decreasing irradiance and temperature. The photodegradation rates of triclosan and OP in Antarctica are predicted to be reduced to below the photodegradation rates observed at the lowest laboratory conditions of 300 W m^{-2} and 7°C. Triclosan was shown to photodegrade 4 – 5 times faster in seawater than OP, and is therefore expected to degrade faster than OP even under Antarctic conditions.

The photodegradation rates will be further decreased by depth and the presence of sea ice. As discussed in Section 5.1.2.4 ~1.4 m of sea ice, or ~15.5 m of open ocean water, is required to reduce the irradiance level to ~10% of its original intensity. Below-ice measurements showed that surface irradiances can be reduced to as low as 1% of its original intensity [312-314]. During the field work conducted over the 2012/2013 season the sea ice thickness measurements ranged between 158 – 229 cm. Maximum irradiance levels in Erebus Bay occur in December, and reaches up to 1010 W m^{-2} (Table 5.1). A maximum of ~100 W m^{-2} is predicted to be able to reach the water column in the presence of sea ice. Sea ice thickness decreases throughout the Antarctic summer from bottom melting, until the ice breaks away [307]. During this period irradiance levels also increase as summer progresses [162]. Under ice-free conditions with increased irradiances the photodegradation rates of triclosan and OP are expected to greatly increase to rates similar to those observed in the laboratory experiments.

The field measurements discussed in Chapter 4 show that the photolabile triclosan and OP were detected only infrequently in the seawaters of Erebus Bay, and at concentrations near or below the LOQ. The photostable micropollutants mParaben, BP-3, and BPA were detected throughout Erebus Bay. The photostable UV filters 4-MBC and OMC [220, 336] were also frequently detected. The concentration ranges of micropollutants detected in the Scott Base WWTP effluents were comparable to each other, and approximately equal amounts of each detected analyte (including triclosan and OP) were released into Erebus Bay. If triclosan and OP were predicted to photo-degrade beneath the sea ice, but with half-lives of at best several days, their seawater concentrations and detection frequencies may be expected to be higher than was observed in the field, assuming photodegradation is the only major process involved in their environmental removal. During the Antarctic summer the levels of UV-B radiation are increased due to the ozone hole [304]. The UV-B spectrum (280 – 320 nm) shares a large overlap of the UV spectrum of triclosan and OP, and may therefore lead to more photodegradation than was measured during the experimentally simulated irradiances (>300 nm, standard procedure). This suggests we may be underestimating the photodegradation potential of triclosan and OP under Antarctic conditions. The importance of photodegradation processes on the fate and behaviour of micropollutants is therefore likely to be analyte-dependent and requires further study.

5.3.8.1 Photodegradation Potential in Whakaraupo Harbour

The irradiance and temperature conditions differ greatly between Erebus Bay and Whakaraupo Harbour, which may give rise to differences in the degradation behaviour, including photodegradation, of the detected micropollutants. Furthermore, as discussed in Chapter 3 the seawater in Whakaraupo Harbour has predominantly zero visibility due to the high suspended sediment content [175]. Photodegradation processes are therefore likely to be restricted within the top water layer of Whakaraupo Harbour.

Average monthly irradiance conditions in Whakaraupo Harbour can be as low as 143 W m^{-2} in June, with up to 200 W m^{-2} under clear sky conditions (Table 5.1). Average mid-day irradiances in June lie at 240 W m^{-2}. These irradiances were not expected to greatly reduce the photodegradation potential of triclosan and OP at the water surface. However photodegradation processes are likely to be inhibited in deeper waters. The waters of Whakaraupo Harbour are well mixed, recirculating any undegraded micropollutants back to the water surface.

Conversely, at the highest summer irradiances (580 W m^{-2} average monthly irradiance, 800 W m^{-2} clear sky irradiances) only limited photodegradation of the more photo-stable analytes such as mParaben, EE2, BPA, or UV filters is expected to occur. Field measurements show

only traces of triclosan and OP in the Whakaraupo seawaters (Chapter 3), while the more photo-stable micropollutants were detected throughout the harbour. These observations match those from Erebus Bay. The limited water visibility in Whakaraupo Harbour may therefore have only a limited effect on the photodegradation potential of micropollutants. Photo-labile micropollutants such as triclosan and OP are therefore expected to readily photodegrade throughout the year, while photo-stable micropollutants are expected to remain stable throughout the year.

5.3.9 Comparisons to Freshwater

Initial photodegradation experiments undertaken at CSIRO Adelaide in 2011 were conducted using freshwater sourced from Wivenhoe Dam lake, Brisbane, Queensland Australia. These photodegradation experiments were carried out under a limited range of irradiances and temperatures, and were therefore not included in the main results and discussion of this chapter. These experiments were carried out in either MQ water or freshwater instead of seawater, and provided data for comparisons to be made to previously published international MQ and freshwater photodegradation data. The photodegradation of BPA, EE2, BP-3, triclosan, and OP were investigated.

Using the same statistical analyses as those used in Section 5.3.6 the trends observed in the freshwater were identical to those observed in the seawater. Only minimal photodegradation of BPA, EE2, and BP-3 was measured in the freshwater. Triclosan and OP readily photodegraded in the freshwater. Measured photodegradation rates were in agreement with those measured internationally in freshwater (Table 5.3 and Table 5.5). The half-lives of triclosan and OP in the freshwater are provided in Table 5.7, and ranged between 0.8 – 2.5 hours for triclosan, and between 1.9 – 16.4 hours for OP. These half-lives compare well to the half-lives measured in the MQ and seawater experiments. The photodegradation of triclosan correlated with irradiance (p = 0.00040) but not with temperature (p = 0.5542). The photodegradation of OP correlated with irradiance (p = 0.0571) and with temperature (p = 0.00128). The degradation of triclosan was significantly enhanced in the freshwater compared to the MQ water (p = 0.00027, Welch Two Sample t-test). The degradation of OP was not enhanced in the freshwater compared to the MQ water (p = 0.7835, Welch Two Sample t-test).

Table 5.7: Experimentally measured half-lives (hours) of triclosan and OP in freshwater from experiments carried out in 2011.

	Triclosan				OP			
	250 W m^{-2}	330 W m^{-2}	500 W m^{-2}	700 W m^{-2}	250 W m^{-2}	330 W m^{-2}	500 W m^{-2}	700 W m^{-2}
7°C	2.1	1.4	0.9	–	13.1	14.1	6.9	–
	2.5	1.5	0.9		16.4	10.5	5.0	
21°C	–	–	–	1.3	–	–	–	4.9
				0.5				3.0
27°C	1.7	–	0.8	–	4.1	–	2.5	–
	1.7		0.9		4.2		1.9	

– = experiments not carried out under these environmental conditions.

These results indicate that seasonal changes of irradiance and temperature in lakes and rivers impacted by WWTP effluents may need to be taken into account when assessing the photodegradation rates of micropollutants.

5.4 Conclusion

BPA, EE2, BP-3, triclosan, and OP have been shown to undergo photodegradation in MQ and seawater. mParaben was shown to remain stable over the experimental exposure period in both types of water. Triclosan and OP are significantly more photo-active than BPA, EE2, and BP-3. Limited degradation of only up to 20% of BPA, EE2, and BP-3 was observed, limiting the conclusions that could be drawn. The half-lives of all compounds fall within the range of previously reported half-lives in MQ water and freshwater.

The main findings for triclosan and OP are:

Triclosan:

- Photodegradation significantly decreases with decreasing irradiance in both MQ and seawater.
- Photodegradation does not significantly decrease with decreasing temperature in MQ and seawater.
- Photodegradation is enhanced in the seawater compared to the MQ water up to 3 – 4 fold, most likely due to effects of pH.
- Identical trends occur in freshwater.

OP:

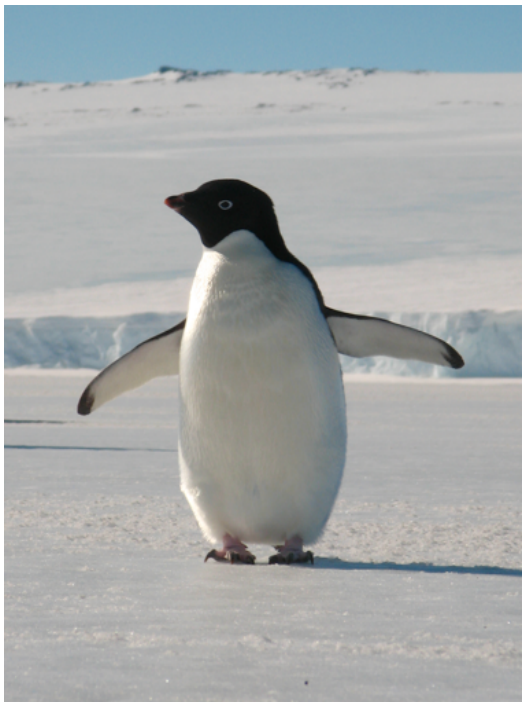
- Photodegradation decreases with decreasing irradiance in MQ and seawater.
- Photodegradation decreases with decreasing temperature in MQ and seawater.
- Photodegradation is not enhanced in the seawater compared to the MQ water.
- Identical trends occur in freshwater.

Under Antarctic conditions the photodegradation of triclosan and OP were predicted to decrease to rates below those observed in the laboratory conditions. Irradiance levels below the Antarctic sea ice are expected to not exceed 100 W m^{-2}. Photodegradation of triclosan and OP may therefore occur, albeit to only a limited extent. Photodegradation half-lives of triclosan and OP expected to remain in the order of several days beneath the sea ice. Field measurements in Erebus Bay show the frequent detection of photo-stable micropollutants such as mParaben, BP-3, and BPA, and the infrequent detection of the photo-labile triclosan and OP. However, due to the release of approximately equal amounts of photo-labile and photo-stable micropollutants into Erebus Bay via WWTP discharges, and the protective effect of the sea ice, the water concentrations and detection frequencies of triclosan and OP were expected to be higher than was observed (Chapter 4). The photodegradation potential of triclosan and OP may therefore be underestimated. Enhanced degradation of triclosan and OP may occur due to the elevated UV-B radiation levels present during the Antarctic summer, which was mostly filtered out during the laboratory experiments according to standard procedures. In New Zealand the photodegradation rates of the studied analytes are expected to remain relatively unaffected by low irradiances and temperatures during the winter months.

The analyte-dependent photodegradation behaviour may have implications for setting regulatory guidelines for acceptable environmental concentrations of micropollutants. Regulatory guidelines and assessment protocols may need to be tailored towards the environmental conditions of the region as well as each analyte.

CHAPTER SIX

FINAL CONCLUSIONS AND RECOMMENDATIONS



6 Final Conclusions and Recommendations

6.1 Overview

The main comparisons and conclusions of the research described in this thesis are presented in the previous chapters. This chapter draws together the research findings in a short and comprehensive discussion on the presence and fate of micropollutants in Whakaraupo Harbour, New Zealand, and Erebus Bay, Antarctica. This chapter also presents the key findings of the research, and suggests recommendations for further research.

6.2 Micropollutants in New Zealand and Antarctica

6.2.1 WWTP Effluents and Coastal Seawater

This study has shown that WWTP effluent discharges into Whakaraupo Harbour and Erebus Bay are a source of micropollutants in the coastal aquatic environment. The most commonly detected micropollutants were OP, 4-MBC, BP-3, BP-1, triclosan, methyl triclosan, BPA, E1, and Cstanol. The effluent concentrations of target analytes were comparable to previously reported international data. Micropollutant concentrations in New Zealand effluents ranged between low to mid ng L^{-1} levels, while in Antarctic research effluent concentrations ranged between low ng L^{-1} to low μg L^{-1} levels. The maximum effluent concentrations of OP, 4-MBC, BP-1, E1, and EE2 detected in the 2012/2013 December sample were higher than what has to date been reported internationally for sewage effluents. The concentrations of most target analytes in the New Zealand WWTP effluents were found to significantly increase in winter compared to summer. This temporal trend was analyte specific and was not observed consistently in all three WWTPs, despite their similar building design. In the effluents of Scott Base during the 2012/2013 season the concentrations of target analytes fluctuated throughout the research season.

In the New Zealand and Antarctic coastal seawaters the concentrations of detected target analytes decreased to near detection limit levels. This drop in concentration can mainly be attributed to the large dilution capacity of the coastal environment. The most commonly detected micropollutants were mParaben, 4-MBC, BP-3, OMC, BPA, and E1. Less commonly detected analytes were OP, BP-1, triclosan, E2, E3, and Cstanol. Whakaraupo Harbour receives sewage effluent from a population of ~5,000 throughout the year, while Erebus Bay receives sewage effluent from a population which for the majority of the year lies below 1,000. Despite this the environmental results for the New Zealand and Antarctic studies were remarkably similar, with the same range of micropollutants detected in both

environments at similar concentration ranges. Furthermore, the coastal seawater concentrations of the detected target analytes were comparable to international data, which were obtained in research areas impacted by much larger population centres. Of the commonly detected target analytes in the sewage effluents, only 4-MBC, BP-3, BPA, and E1 were also commonly detected in the seawater of Whakaraupo Harbour and Erebus Bay. OP, BP-1, triclosan, methyl triclosan, and Cstanol were detected only infrequently. The target analytes mParaben and OMC were frequently detected in the seawaters but not in the sewage effluents in both the New Zealand and Antarctic studies. The reasons for this are currently unknown. Micropollutants were detected throughout the New Zealand and Antarctic study areas, including the New Zealand reference site at Pigeon Bay, and the Antarctic reference sites at Cape Evans, 25 up-current from the research station WWTP discharge points. Much larger coastal areas are therefore impacted than was previously thought, particularly in Antarctica. This shows we do not yet fully understand the distribution mechanisms of sewage-derived pollutants in the marine environment and raises interesting questions as to why such a vastly different environment can be equally polluted.

6.2.2 Marine Sediments

The marine sediments of Whakaraupo Harbour were found to be a sink of micropollutants. The same target analytes detected in the seawater were also detected in the marine sediments, namely mParaben, OP, 4-MBC, BP-3, BP-1, BPA, OMC, E1, and Cstanol. Measured concentrations were in the low ng g^{-1} dry weight range, and in the lower range of previously reported international data. The distribution of target analytes throughout Whakaraupo Harbour and their concentrations within the sediments varied between the two sampling rounds conducted in April and October 2012. This was attributed to the well-flushed nature of the harbour and the high sedimentation rates. The marine sediments in Erebus Bay could not be sampled due to fieldwork restrictions. However, Antarctic marine sediments were concluded to be a likely sink of micropollutants.

6.2.3 Marine Biota

Micropollutants were found to bioaccumulate in marine biota from Whakaraupo Harbour and Erebus Bay. New Zealand green lipped mussels (*Perna canalicula*) collected in Whakaraupo Harbour were found to bioaccumulate mParaben, OP, and BP-3. A wider range of target analytes were detected in the Antarctic biota. The clams (*Laternula elliptica*) were found to bioaccumulate mParaben, pParaben, BP-3, E2, EE2, and Cstanol. The analytes mParaben, BP-3, and Cstanol bioaccumulated in the sea urchins (*Sterichinus neumayeri*). The fish (*Trematomus bernachii*) bioacummulated mParaben, OP, and BP-3, while a fish liver sample was found to bioaccumulate mParaben and BP-3. Overall concentrations ranged between low

to mid ng g^{-1} dry weight concentrations. Only limited international data exists on the bioacummulation of the detected target analytes. The tissue concentrations of OP, BP-3, and EE2 are comparable to previously reported international data. However some tissue concentrations of BP-3 exceed previously reported international data four-fold. This study is the first to report on the bioaccumulation of mParaben, pParaben, and E2 in environmental samples.

The highest concentrations of BP-3 were detected in the Antarctic clam tissues (112 ng g^{-1} d.w.), while the highest concentrations of mParaben were detected in the Antarctic fish muscle tissues (26.9 ng g^{-1} d.w.). The concentrations of BP-3 in fish were higher in the liver (41 ng g^{-1} d.w.) than the maximum muscle tissue concentration (14.1 ng g^{-1} d.w.). This suggests the bioaccumulation of some micropollutants is species and tissue specific. The tissue concentrations of mParaben in the fish correlated negatively with fish fillet weight (R^2 = 0.6613, p = 0.026).

Due to matrix interferences acceptable spike recoveries were only achieved for mParaben, eParaben, OP, pParaben, BP-3, E2, EE2, and E3. It is probable that with improved extraction and clean-up steps adequate recoveries of the remaining target analytes could be achieved. Because of their presence in the harbour waters and sediments it is likely the other micropollutants such as 4-MBC, OMC, and BPA are also present in biota.

6.2.4 Comparisons Between Whakaraupo Harbour and Erebus Bay

The presence and distribution of micropollutants in the Whakaraupo Harbour and Antarctic studies were highly comparable. The same range of micropollutants were detected in the sewage effluents, seawater, and biota in both environments. However the maximum concentrations of micropollutants in sewage effluents were higher in the 2012/2013 Scott Base sewage effluents than the New Zealand sewage effluents. Month to month concentration fluctuations were also greater in Antarctica. These differences can be attributed to the less stable environmental conditions (temperature, inflow volumes, etc) inside the WWTP of Scott Base compared to the WWTPs in Whakaraupo Harbour. The seawater data are more comparable between the two study areas than the sewage effluent data, however the 2009/2010 Antarctic seawater concentrations were higher compared to the Whakaraupo Harbour study. However overall trends were similar. The concentrations of detected target analytes were equally distributed around both coastal areas. Furthermore the target analytes mParaben and OMC were detected in both coastal areas, but not their respective sewage effluents. Lastly, a wider range of micropollutants were found to bioaccumulate in the Antarctic biota compared to the New Zealand biota. However this may be due to the fact that three marine species from Antarctica were analysed, while only one marine species was

sampled from New Zealand. The measured biota concentrations were comparable between the two environments. These overall highly comparable results between two otherwise extremely different environments suggests that environmental conditions such as temperature, sunlight, and sea ice cover, have only minor impacts on the distribution and fate of micropollutants.

6.3 Photodegradation as a Key Environmental Removal Process

The photodegradation of the micropollutants mParaben, OP, BP-3, triclosan, BPA, and EE2 was investigated under a range of irradiance and temperature conditions. BPA, EE2, and BPA showed only minor photodegradation over the solar exposure period, even at the highest irradiance and temperature settings, while mParaben remained completely stable at all environmental conditions. Only triclosan and OP were found to readily photodegrade under all environmental conditions. The photodegradation rate of triclosan was found to significantly decrease with decreasing irradiance intensity. Triclosan degradation was found to be significantly enhanced in seawater compared to MilliQ water. The photodegradation rate of OP was found to significantly decrease with both decreasing irradiance intensity and temperature. The photodegradation of OP was not enhanced in the seawater.

These results help explain the observed occurrence of micropollutants in the New Zealand and Antarctic coastal seawaters. The photo-stable target analytes BPA and BP-3, which were frequently detected in the sewage effluents, were also commonly detected in the seawaters. E1, which is structurally closely related to the photo-stable EE2, was also commonly detected in both the sewage effluents and the seawater. While mParaben was not frequently detected in the sewage effluents, it was frequently detected in the seawaters. Upon its release via as yet unidentified sources it remains in the water phase, most likely due to its high photostability. Conversely, while the photo labile triclosan and OP were frequently detected in the sewage effluents they were only infrequently detected in the seawater. The detection of each of the target analytes in Whakaraupo Harbour and Erebus Bay, or lack thereof, can therefore be explained by its capacity for photodegradation.

6.4 Environmental Implications

The high concentrations of micropollutants in the WWTP effluents of Scott Base are of concern, having been observed to reach low $\mu g\ L^{-1}$. The high concentrations of alkylphenols, UV filters, and triclosan are of particular concern as they may affect the microbial communities of the WWTP biofilm and affecting the treatment efficiency.

Direct exposure of marine organisms to the low $ng\ L^{-1}$ concentrations of micropollutants detected in the seawaters of Whakaraupo Harbour and Erebus Bay are likely to pose only

limited risks. As discussed in Chapter 3, previously published exposure studies of the target analytes detected in the seawaters report the occurrence of biological effects at concentrations orders of magnitude above environmental levels. However, these micropollutants may still pose a risk to the marine environment due to their potential for accumulation in marine sediments and biota, promoted by their continuous presence in the aqueous phase. Despite the well-flushed nature of Whakaraupo Harbour micropollutants were found to accumulate in marine sediments. Concentrations of OP and BPA have at some locations reached levels at which biological effects have been reported. It is likely Antarctic marine sediments are also a sink of micropollutants. The accumulation of micropollutants in marine sediments may also promote their bioaccumulation in sediment-dwelling organisms. The filter-feeding New Zealand green-lipped mussel has been found to bioaccumulate mParaben, OP, and BP-3. It is likely other marine organisms also bioaccumulate micropollutants. This theory is supported by the detection of mParaben, pParaben, OP, BP-3, E2, EE2, and Cstanol in clams, sea urchins, and fish from Antarctica. The observed presence of micropollutants in this wide range of marine organisms suggests that organisms may also become exposed to micropollutants via the dietary route as well as exposure through contact with polluted sediments.

The observed bioaccumulation of mParaben and pParaben in the Antarctic biota is of particular concern. Based on their K_{OW} values (1.66 and 2.71 respectively) bioaccumulation of these micropollutants is not expected. This suggests a wider range of micropollutants may be of environmental concern than previously thought. Antarctic biota generally have very slow metabolisms and are slow growing [278]. This is likely to reduce the excretion rates of potentially harmful chemicals, leading to longer *in vivo* exposure periods. Critical periods of biological development may also be longer than in other aquatic organisms. During this time endocrine disruption may have a particularly severe detrimental effect. Antarctic biota may therefore be particularly sensitive to the effects of micropollutants.

The wide distribution of micropollutants in seawater, sediments, and biota in Whakaraupo Harbour and Erebus Bay shows that a much larger coastal area may be impacted by sewage effluent discharges than previously thought. Photodegradation processes may reduce the risks of photo-labile chemicals such as triclosan and OP, but not photostable chemicals such as mParaben, BPA, EE2, and BP-3. The photo-labile micropollutants triclosan and OP were predicted to remain stable under the low irradiance and temperature effects which occur under the sea ice in Erebus Bay, potentially reaching concentrations similar to those measured for mParaben, BPA, or the UV filters. However, field measurements show the overall absence of triclosan and OP in the water column. The photodegradation potential of triclosan and OP

may have therefore been underestimated, or other unidentified degradation processes may need to be considered.

6.5 Recommendations for Future Research

As highlighted by Ort *et al* [337] concentrations of micropollutants in sewage influents and effluents cannot be assumed to remain constant with time. While concentration fluctuations in effluents are less than in influents, these effluent fluctuations must still be considered during sampling. The collection of grab samples as was done for this thesis was therefore not the most optimal method for evaluating the temporal and plant-to-plant variations in micropollutant concentrations in the Whakaraupo Harbour and Erebus Bay studies. Ort *et al* [337] recommended preliminary high sampling frequency (sampling every 15 – 30 minutes) to determine micropollutant concentration fluctuations. Such a high sampling rate would be prohibitively expensive. More optimal but sophisticated sampling modes such as continuous or discrete flow- or time-proportional sampling should be considered in future studies.

The method used for the extraction and analysis of the biota samples was not sensitive enough to allow for the quantification of several target analytes, including triclosan, methyl triclosan, 4-MBC, BPA, and OMC. Their potential for bioaccumulation has been identified, and these compounds are likely present in the marine biota from Whakaraupo Harbour and Erebus Bay. The extraction and analysis method should therefore be improved, and the marine samples re-extracted and re-analysed. A wider range of marine species from Whakaraupo Harbour should also be analysed, such as sediment-dwelling organisms and fish, to allow for better comparisons to the Antarctic marine data to be made.

The regular detection of mParaben and OMC in the seawater samples of Whakaraupo Harbour and Erebus Bay, but not the sewage effluents discharged into these coastal areas, should be investigated. The Christchurch City ocean sewage outfall has been identified as a potential source in Whakaraupo Harbour, and the practice of tide-cracking and McMurdo Station have been identified as a potential source in Erebus Bay. Other as yet unidentified pathways for the entry of micropollutants into the marine environment may also play a role.

The environmental fate and behaviour of the paraben preservatives requires further research. Their unexpected bioaccumulation in marine biota makes them micropollutants of environmental importance. The potential for dietary exposure of micropollutants has been identified, and feeding off impacted fish may impact other species such as marine mammals. Non-invasively collected samples of Weddell seal urine, which is commonly found on the sea ice around Erebus Bay and which was collected during the 2009/2010 research season, may show traces of micropollutant exposure.

The large areas of coastal habitat found to be impacted by micropollutants shows a much larger area is affected by anthropogenic impacts than previously thought. The full extent to which this pollution can migrate away from the pollution sources should be investigated to allow for better environmental impact assessments to be made. This is particularly important in Antarctica where environmental impacts are regularly assessed and monitored.

The high loading of micropollutants in the sewage effluents of Scott Base is of concern. Due to its small size the treatment efficiency of the Scott Base WWTP fluctuates throughout the year. Research on the treatment efficiency of the WWTP, such as improving the effectiveness of the ozone disinfection plant, would greatly reduce the environmental impacts on the coastal environment.

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8 Appendix A

Table 8.1: Analytes (ng L^{-1}) detected in Whakaraupo Harbour during the SPE method validation.

Analyte	03Nov2010	19Nov2010	30Nov2010	21Sept2011	5Oct2011	18Oct2011
	4 L	10 L	10 L	4 L	4 L	10 L
mParaben	4.3	9.3	7.7	1.2	1.6	2.5
eParaben	–	–	–	–	–	–
OP	0.3	0.30	0.3	0.5	0.70	0.5
pParaben	1.5	5.40	2.5	–	–	–
bParaben	–	–	–	–	–	–
NP	–	–	–	–	–	–
4-MBC	–	–	5.7	3.8	5.1	<3.2
BP-3	3.8	10.4	11.0	<2.6	3.3	<2.6
mTric	–	–	–	–	–	–
Tric	–	0.5	1.0	–	–	–
BP-1	–	<0.8	–	–	–	–
BPA	5.7	3.1	3.2	9.7	4.0	4.4
OMC	–	<1.9	3.5	–	–	–
E1	–	–	–	<7.0	<7.0	–
E2	–	–	–	–	–	–
EE2	–	–	–	–	–	–
E3	–	–	–	<2.1	<2.1	–
mParaben (ring $^{13}C_6$)	92.2%	90.4%	94.7%	84.7%	80.9%	89.7%
bParaben (ring $^{13}C_6$)	108.0%	94.5%	97.9%	83.9%	88.0%	91.4%
NP (ring $^{13}C_6$)	57.8%	58.4%	62.0%	57.4%	56.5%	68.3%
Tric (ring $^{13}C_{12}$)	118.5%	93.4%	101.9%	107.8%	102.1%	99.2%
BPA (ring $^{13}C_{12}$)	85.7%	73.0%	73.4%	92.3%	91.6%	77.7%
E2 (ring $^{13}C_6$)	95.1%	70.6%	74.9%	88.6%	91.7%	68.0%

Table 8.2: Analytes (ng L^{-1}) detected in the sewage effluents of the Lyttelton, Governors Bay, and Diamond Harbour WWTPs.

Analyte		24th Jan	24th Jan	2nd April	2nd April	7th May	7th May	5th June	5th June	2nd July	2nd July	6th Aug	6th Aug
mParaben	Lyttelton	–	–	1.6	1.0	3.3	3.6	1.6	1.2	–	–	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	–	–	–	–	1.4	0.9	–	–	–	–	–	–
4NP	Lyttelton	22.9	19.9	23.5	24.7	29.8	35.1	42.3	38.1	69.2	71.3	290.0	301.8
	Governors	–	–	35.4	35.6	31.7	31.6	47.0	40.4	38.0	32.0	41.7	39.9
	Diamond	–	–	18.0	16.0	20.4	17.4	21.8	18.7	23.1	25.2	23.7	19.9
eParaben	Lyttelton	–	–	4.0	4.1	–	–	–	–	–	–	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	–	–	–	–	7.0	6.8	–	–	–	–	–	–
OP	Lyttelton	–	–	5.7	4.7	11.2	10.0	16.1	16.1	51.8	47.6	18	17.1
	Governors	–	–	8.6	8.5	6.7	6.6	4.6	4.7	10.4	11.4	4.7	4.5
	Diamond	–	–	4.9	4.9	4.8	4.2	6.1	4.3	8.3	8.1	5.8	5.5
pParaben	Lyttelton	–	–	–	–	–	–	–	–	–	–	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	–	–	–	–	–	–	–	–	–	–	–	–
bParaben	Lyttelton	5.3	6.4	–	–	–	–	–	–	–	–	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	–	–	–	–	–	–	–	–	–	–	–	–
NP	Lyttelton	–	–	–	–	–	–	–	–	–	–	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	–	–	–	–	–	–	–	–	–	–	–	–
4-MBC	Lyttelton	66.9	46.8	76.7	66.8	79.0	70.1	99.1	91.6	210.4	195.2	138.5	130.0
	Governors	122.9	104.0	111.9	110.7	76.7	80.4	155.4	154.6	153.9	145.3	96.8	95.2
	Diamond	366.0	363.5	160.9	154.6	78.5	77.1	95.0	88.5	112.8	112.9	72.4	63.8
BP-3	Lyttelton	29.1	11.0	33.6	20.8	33.7	22.9	22.9	19.0	50.2	45.6	164.8	155.1
	Governors	35.6	33.7	50.8	47.2	24.0	22.8	25.5	25.2	38.0	29.4	43.9	39.4
	Diamond	50.3	207.3	46.9	47.4	25.4	22.8	38.6	35.2	39.1	39.1	113.2	98.2

mTric	Lyttelton	–	8.8	7.2	6.8	8.8	7.0	15.3	14.8	35.3	34.0	–	–
	Governors	8.6	6.3	–	–	9.3	10.5	9.7	12.3	6.8	–	–	–
	Diamond	15.2	14.0	14.0	13.4	11.4	11.8	14.6	14.4	13.2	11.5	5.2	5.7
Triclosan	Lyttelton	25.6	25.5	22.3	20.3	26.0	23.5	40.9	37.4	54.3	50.9	121.5	118.0
	Governors	13.8	14.1	33.2	33.1	32.8	33.5	56.1	53.3	44.2	42.8	32.6	29.6
	Diamond	31.8	31.0	26.7	27.0	20.7	20.3	30.1	31.3	39.5	38.8	41.1	37.0
BP-1	Lyttelton	5.3	5.2	6.7	6.2	18.2	11.6	17.8	19.3	29.8	28.0	61.2	57.9
	Governors	8.9	7.8	14.6	15.1	10.6	10.2	12.7	12.9	15.2	13.8	10.4	10.8
	Diamond	84.9	87.3	35.3	35.9	19.5	18.7	45.7	44.5	24.2	22.0	67.2	57.1
BPA	Lyttelton	4.6	3.8	7.5	10.2	8.1	7.2	18.6	19.0	122.8	125.9	165.3	160.5
	Governors	36.6	6.7	20.8	22.4	22.6	22.3	28.9	27.5	66.3	69.8	46.4	47.8
	Diamond	13.1	16.1	8.2	8.7	7.5	5.7	20.0	20.0	27.6	26.6	43.2	38.0
OMC	Lyttelton	–	–	–	–	–	–	–	–	–	–	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	–	–	–	–	–	–	–	–	–	–	–	–
E1	Lyttelton	–	–	28.4	30.6	38.5	33.7	21.2	20.6	78.4	74.8	22.6	23.4
	Governors	41.6	62.7	38.4	38.2	–	–	37.9	41.8	7.9	6.2	2.1	2.1
	Diamond	–	–	16.9	15.4	–	–	10.6	11.1	20.6	18.3	4.0	4.1
E2	Lyttelton	–	–	–	–	–	–	–	–	18.8	18.8	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	–	–	–	–	–	–	–	–	–	–	2.8	3.9
Cstane	Lyttelton	–	–	–	–	–	–	–	–	–	–	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	–	–	–	–	–	–	–	–	–	–	–	–
EE2	Lyttelton	–	–	–	–	–	–	–	–	13.2	13.0	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	–	–	–	–	–	–	–	–	–	–	–	–
E3	Lyttelton	–	–	–	–	–	–	–	–	11.3	10.5	–	–
	Governors	–	–	–	–	–	–	–	–	–	–	–	–
	Diamond	6.3	6.7	–	–	–	–	–	–	–	–	2.6	2.7

Cstanol	Lyttelton	11.3	10.6	75.0	75.3	117.7	109.1	99.0	88.4	255.5	236.0	491.0	867.1
	Governors	47.0	36.5	54.6	53.9	80.6	75.1	71.7	79.7	222.8	108.3	46.1	48.6
	Diamond	49.7	57.8	69.5	67.1	81.2	83.1	58.7	62.1	123.7	121.2	177.3	173.6

ND = not detected

Table 8.2 continued: Analytes (ng L^{-1}) detected in the sewage effluents of the Lyttelton, Governors Bay, and Diamond Harbour WWTPs.

Analyte		31st Aug	31st Aug	2nd Oct	2nd Oct	6th Nov	6th Nov	4th Dec	4th Dec	8th Jan	8th Jan	Literature range, (ng/L)	Reference
mParaben	Lyttelton	1.4	1.8	–	–	–	–	–	–	–	–	2.1 – 423	[47-49]
	Governors	2.2	1.8	–	–	–	–	–	–	–	–		
	Diamond	4.4	4.9	–	–	–	–	19.6	21.2	–	–		
4NP	Lyttelton	16.8	16.4	20.6	22.3	28.0	34.0	57.7	81.6	31.2	28.8	2540	[338]
	Governors	30.4	27.2	15.9	14.3	18.6	12.1	38.5	34.4	–	–		
	Diamond	57.6	76.2	59.5	45.5	31.3	33.0	156.4	162.8	30.1	25.0		
eParaben	Lyttelton	–	–	–	–	–	–	–	–	–	–	<0.3 – 69	[47, 49,
	Governors	–	–	–	–	–	–	6.5	6.5	–	–		50]
	Diamond	–	–	–	–	–	–	–	–	–	–		
OP	Lyttelton	35.9	33.9	205.8	170.8	54.3	59.1	11.3	11.9	10.8	8.8	1.2 – 470	[47, 51]
	Governors	5.9	4.6	5.4	5.7	8.6	6.5	7.7	7.4	5.4	2.3		[54]
	Diamond	7.5	8.3	14.4	13.0	7.9	9.1	20.6	22.4	15.6	14.4		
pParaben	Lyttelton	–	–	–	–	–	–	–	–	–	–		
	Governors	–	–	–	–	–	–	–	–	–	–		
	Diamond	–	–	–	–	–	–	50.8	47.6	–	–		
bParaben	Lyttelton	–	–	–	–	–	–	–	–	–	–	<0.2 – 83	[46, 47,
	Governors	–	–	–	–	–	–	–	–	–	–		50, 51]
	Diamond	–	–	–	–	–	–	8.3	7.3	–	–		
NP	Lyttelton	–	–	–	–	–	–	–	–	–	–		
	Governors	–	–	–	–	–	–	–	–	–	–		
	Diamond	–	–	–	–	–	–	–	–	–	–		
4-MBC	Lyttelton	90.0	75.5	85.4	74.5	28.2	23.2	32.0	32.8	72.3	64.7	42 – 2300	[56, 58]
	Governors	69.3	59.3	56.5	54.1	93.8	86.2	89.9	81.3	89.2	73.4		
	Diamond	174.0	208.3	110.8	89.2	78.2	84.8	160.8	159.3	428.8	413.5		
BP-3	Lyttelton	43.3	39.4	59.3	53.5	36.6	35.7	52.5	55.4	51.2	38.9	3 – 2,196	[49, 55,

	Governors	30.0	26.5	35.0	31.9	35.1	29.4	89.3	84.6	30.6	23.9		56]
	Diamond	122.2	136.9	130.4	117.0	83.7	91.4	170.0	169.6	101.7	91.4		
mTric	Lyttelton	13.6	12.7	14.2	11.9	–	2.7	–	–	4.3	3.4	<2 – 51	[63, 64]
	Governors	–	–	–	–	4.1	3.8	4.5	3.6	6.7	7.6		
	Diamond	–	–	–	–	6.4	6.8	5.8	6.3	7.0	7.4		
Triclosan	Lyttelton	29.4	28.4	30.6	27.5	17.5	15.4	13.1	14.3	18.5	17.7	0.4 –	[54, 185,
	Governors	22.5	21.7	18.8	18.5	21.4	19.7	21.7	20.6	21.0	18.8	1120	186]
	Diamond	108.6	98.3	38.6	34.8	16.7	19.0	24.1	24.4	16.7	17.3		
BP-1	Lyttelton	12.3	12.3	9.2	7.8	5.0	5.2	5.3	5.6	5.4	3.6	<2 – 41	[49, 59,
	Governors	8.2	8.4	6.6	7.0	8.1	7.8	19.6	18.2	7.1	7.6		61]
	Diamond	63.6	63.6	46.1	44.5	27.7	31.5	146.2	143.8	61.3	58.8		
BPA	Lyttelton	49.7	47.2	57.3	62.5	94.9	77.6	–	–	5.2	4.1	1.3 –	[47, 51,
	Governors	29.9	28.6	16.5	15.4	29.5	–	4.8	3.5	7.6	7.3	2600	53]
	Diamond	62.4	63.4	38.2	41.1	–	17.0	46.3	43.2	10.1	13.7		
OMC	Lyttelton	–	–	–	–	–	–	–	–	–	–		
	Governors	–	–	–	–	–	–	–	–	–	–		
	Diamond	–	–	–	–	–	–	–	–	–	–		
E1	Lyttelton	5.3	5.2	2.4	2.4	2.7	2.4	3.5	4.2	–	–	1 – 110	[51, 54]
	Governors	9.7	9.5	42.4	43.5	6.6	8.3	36.7	34.3	–	–		
	Diamond	4.3	4.7	22.6	21.9	11.7	13.1	110.8	113.8	36.6	32.0		
E2	Lyttelton	–	–	–	–	–	–	–	–	–	–	0.2 – 158	[66]
	Governors	–	–	–	–	–	–	–	–	–	–		
	Diamond	–	–	–	–	–	–	–	–	1.3	1.3		
Cstane	Lyttelton	–	–	–	–	–	–	–	–	–	–		
	Governors	–	–	–	–	–	–	–	–	–	–		
	Diamond	–	–	–	–	–	–	–	–	–	–		
EE2	Lyttelton	–	–	–	–	–	–	–	–	–	–	<0.3 – 7.5	[65]
	Governors	–	–	–	–	–	–	–	–	–	–		
	Diamond	–	–	–	–	–	–	–	–	–	–		
E3	Lyttelton	–	–	1.6	<0.6	–	–	–	–	–	–	0.43 –	[66]
	Governors	–	–	–	–	–	–	–	–	–	–	275	
	Diamond	8.9	8.5	1.4	1.1	–	–	6.6	6.1	–	–		
Cstanol	Lyttelton	73.1	56.4	100.4	111.2	38.6	53.7	46.7	70.3	69.9	65.6	N/A	
	Governors	199.1	459.6	15.7	30.3	53.3	58.4	66.4	77.2	27.2	45.9		
	Diamond	258.6	315.7	81.5	78.5	130.9	120.5	286.4	269.1	172.4	167.5		

Table 8.3: Surrogate recoveries and statistical summary of each sewage effluent sample from the Lyttelton, Governors Bay, and Diamond Harbour WWTPs.

Surrogate		24th Jan	24th Jan	2nd April	2nd April	7th May	7th May	5th June	5th June	2nd July	2nd July	6th Aug	6th Aug
mParaben (ring $^{13}C_6$)	Lyttelton	101.8%	100.0%	72.9%	73.0%	81.2%	77.8%	78.8%	73.5%	94.1%	95.6%	119.8%	124.0%
	Governors	88.3%	91.5%	74.0%	76.4%	75.3%	75.1%	74.5%	73.7%	78.9%	87.9%	117.7%	121.2%
	Diamond	100.5%	104.3	75.3%	72.8%	73.0%	76.6%	70.5%	67.7%	75.4%	77.5%	117.2%	106.1%
bParaben (ring $^{13}C_6$)	Lyttelton	102.5%	95.5%	76.8%	79.5%	80.3%	83.3%	76.7%	72.7%	92.8%	85.8%	106.6%	102.5%
	Governors	93.0%	95.7%	71.9%	74.2%	83.5%	82.4%	79.7%	77.4%	86.1%	88.7%	110.3%	109.4%
	Diamond	91.6%	101.9%	77.2%	78.2%	83.4%	84.2%	71.6%	70.1%	76.2%	75.9%	104.2%	88.4%
NP (ring $^{13}C_6$)	Lyttelton	93.3%	97.5%	49.9%	56.1%	54.8%	51.6%	50.6%	50.9%	60.9%	61.6%	85.9%	70.4%
	Governors	149.4%	151.9%	49.4%	54.1%	63.2%	61.8%	56.4%	60.2%	55.9%	54.6%	72.6%	59.0%
	Diamond	105.9%	111.5%	60.4%	55.2%	59.7%	71.9%	52.1%	63.9%	56.9%	54.4%	81.5%	72.5%
Tric (ring $^{13}C_{12}$)	Lyttelton	123.3%	118.1%	64.9%	66.3%	81.0%	72.6%	75.0%	71.0%	89.4%	86.5%	171.6%	145.2%
	Governors	124.9%	117.3%	63.3%	63.2%	72.5%	70.3%	87.0%	90.6%	87.7%	93.0%	152.7%	146.9%
	Diamond	115.3%	117.8%	66.0%	66.5%	68.1%	73.0%	82.5%	81.3%	80.2%	84.8%	149.9%	129.1%
BPA (ring $^{13}C_{12}$)	Lyttelton	90.5%	92.3%	64.8%	65.1%	71.5%	70.9%	59.4%	60.3%	74.5%	74.7%	110.1%	105.8%
	Governors	87.4%	90.8%	60.7%	66.2%	72.5%	70.5%	70.7%	69.5%	73.0%	77.9%	115.0%	118.8%
	Diamond	85.0%	90.4%	63.7%	64.5%	69.9%	70.0%	70.3%	67.4%	75.0%	76.0%	132.6%	109.4%
E2 (ring $^{13}C_6$)	Lyttelton	78.8%	79.6%	88.0%	89.7%	83.9%	77.9%	56.5%	53.0%	74.2%	73.4%	91.9%	89.8%
	Governors	79.8%	71.9%	87.1%	90.3%	88.1%	88.5%	67.1%	66.5%	75.1%	78.9%	92.3%	88.1%
	Diamond	77.0%	79.7%	91.0%	89.0%	90.3%	90.2%	64.6%	63.8%	36.2%	75.1%	84.6%	77.9%

Table 8.3 continued: Surrogate recoveries and statistical summary of each sewage effluent sample from the Lyttelton, Governors Bay, and Diamond Harbour WWTPs.

Surrogate		31st Aug	31st Aug	2nd Oct	2nd Oct	6th Nov	6th Nov	4th Dec	4th Dec	8th Jan	8th Jan	Average	Std dev	%RSD	95% CI
mParaben (ring $^{13}C_6$)	Lyttelton	101.7%	108.6%	127.2%	103.1%	162.2%	168.5%	117.9%	130.9%	155.3%	139.2%	106.6%	29.5%	27.7%	7.3%
	Governors	106.5%	100.4%	113.1%	114.6%	174.3%	165.8%	134.3%	131.7%	134.0%	130.4%				
	Diamond	86.6%	110.7%	111.7%	109.2%	165.7%	172.9%	134.9%	140.4%	120.5%	118.5%				
bParaben (ring $^{13}C_6$)	Lyttelton	102.5%	115.2%	124.2%	93.6%	112.0%	113.3%	105.0%	112.5%	150.6%	128.7%	99.4%	19.5%	19.6%	4.8%
		103.5%	89.3%	131.2%	134.6%	120.9%	129.9%	134.2%	128.1%	119.1%	118.7%				

	Governors	87.7%	93.5%	101.1%	96.9%	121.6%	127.3%	107.6%	112.8%	117.6%	105.5%				
	Diamond														
NP (ring $^{13}C_6$)	Lyttelton	67.9%	59.7%	90.4%	80.8%	119.1%	126.4%	95.9%	98.0%	119.0%	102.5%	81.1%	27.1%	33.4%	6.7%
	Governors	62.1%	59.7%	89.1%	87.7%	128.5%	106.5%	88.3%	68.0%	108.8%	95.5%				
	Diamond	73.0%	72.2%	87.4%	95.0%	139.1%	147.8%	98.6%	98.8%	90.0%	79.9%				
Tric (ring $^{13}C_{12}$)	Lyttelton	130.3%	120.5%	127.3%	111.8%	139.7%	149.4%	89.3%	99.3%	120.6%	113.9%	106.6%	28.0%	26.2%	6.9%
	Governors	118.5%	114.8%	115.9%	110.9%	159.8%	146.7%	105.3%	108.0%	113.0%	112.6%				
	Diamond	116.7%	127.6%	113.1%	112.7%	147.2%	152.1%	104.9%	97.1%	108.6%	99.3%				
BPA (ring $^{13}C_{12}$)	Lyttelton	97.1%	91.6%	93.4%	101.0%	92.4%	102.3%	54.3%	84.2%	84.9%	78.5%	83.0%	16.0%	19.3%	3.9%
	Governors	93.9%	94.5%	96.4%	88.9%	99.8%	73.8%	89.2%	72.8%	89.5%	68.7%				
	Diamond	95.4%	99.5%	84.5%	89.2%	73.1%	99.8%	80.1%	77.9%	64.6%	76.9%				
E2 (ring $^{13}C_6$)	Lyttelton	81.0%	78.7%	94.0%	80.8%	97.5%	98.7%	112.4%	116.5%	140.7%	126.9%	89.3%	19.1%	21.4%	4.7%
	Governors	81.6%	80.8%	90.5%	85.1%	95.2%	99.8%	132.4%	120.5%	118.0%	123.0%				
	Diamond	85.2%	85.5%	86.6%	88.0%	93.8%	100.9%	114.4%	116.4%	119.1%	118.3%				

Table 8.4: Analyte and surrogate spike recovery of the Governors Bay quality control spikes.

Analyte	24th Jan	2nd April	7th May	5th June	2nd July	6th Aug	31st Aug	2nd Oct	6th Nov	4th Dec	8th Jan
mParaben	106.0%	72.6%	77.7%	82.6%	91.2%	110.5%	104.4%	119.0%	147.6%	141.6%	130.1%
eParaben	107.7%	65.4%	68.9%	73.0%	84.9%	104.2%	104.8%	117.4%	134.3%	121.2%	115.8%
OP	107.0%	76.1%	62.9%	93.9%	123.2%	105.1%	76.1%	116.5%	251.0%	115.6%	116.5%
pParaben	125.4%	77.2%	78.3%	82.9%	93.0%	95.9%	102.9%	110.5%	119.6%	125.8%	120.5%
bParaben	90.4%	58.9%	62.9%	62.9%	69.9%	81.7%	75.6%	99.5%	101.6%	108.0%	110.5%
NP	126.6%	45.6%	58.1%	54.3%	62.6%	75.3%	54.6%	69.8%	79.6%	91.5%	110.1%
4-MBC	133.7%	69.8%	67.8%	76.9%	72.0%	112.6%	86.6%	115.0%	152.6%	107.5%	126.4%
BP-3	115.3%	67.6%	65.5%	82.4%	81.3%	120.1%	143.3%	131.0%	139.9%	105.1%	116.6%
mTric	105.0%	63.0%	61.3%	72.4%	83.7%	104.1%	84.0%	118.8%	112.0%	98.7%	92.1%
Triclosan	116.4%	49.3%	55.8%	83.7%	107.4%	121.9%	106.4%	119.3%	128.1%	92.9%	99.4%

BP-1	109.7%	67.1%	76.2%	85.9%	82.7%	116.9%	156.9%	120.2%	106.9%	100.7%	110.1%
BPA	75.8%	52.0%	64.4%	68.1%	76.1%	90.2%	90.1%	91.8%	80.2%	69.7%	55.3%
OMC	91.3%	89.8%	88.0%	72.9%	78.4%	73.9%	77.9%	82.9%	92.6%	107.7%	107.3%
E1	147.8%	203.3%	172.4%	88.7%	106.9%	152.7%	120.4%	131.2%	141.9%	157.6%	194.8%
E2	94.6%	105.5%	102.8%	70.6%	98.5%	93.0%	83.8%	85.6%	93.5%	127.3%	128.7%
EE2	115.6%	127.7%	119.2%	94.6%	108.0%	111.5%	102.9%	117.0%	116.4%	183.0%	180.8%
E3	94.5%	81.0%	91.1%	81.9%	97.2%	103.5%	96.0%	121.8%	104.0%	140.7%	153.0%
mParaben (ring $^{13}C_6$)	100.5%	69.9%	80.3%	78.7%	85.2%	101.8%	98.7%	108.4%	146.6%	110.6%	119.2%
bParaben (ring $^{13}C_6$)	91.1%	74.4%	82.8%	80.7%	83.3%	96.4%	88.0%	116.1%	112.8%	109.7%	110.0%
NP (ring $^{13}C_6$)	176.7%	59.1%	61.2%	53.4%	58.4%	68.1%	46.7%	83.6%	122.5%	87.3%	96.0%
Tric (ring $^{13}C_{12}$)	133.6%	65.4%	74.3%	87.8%	98.1%	137.9%	119.1%	94.8%	132.8%	82.3%	101.5%
BPA (ring $^{13}C_{12}$)	84.3%	57.0%	71.7%	73.3%	81.9%	94.7%	90.9%	85.5%	91.9%	55.2%	54.8%
E2 (ring $^{13}C_6$)	85.6%	94.3%	96.0%	67.3%	83.1%	87.1%	79.8%	93.4%	94.3%	112.7%	126.5%

Table 8.5: Analyte concentrations (ng L^{-1}) and analyte spike recovery of target analytes detected in Whakaraupo Harbour seawater and the Pigeon Bay reference site during the April, July, October, and January sampling rounds, plus the offshore sample collected in April.

Analyte	Month	Site 1	Site 2	Site 2 Spike	Site 3	Site 4	Site 5	Site 6	Site 6 duplicate	Site 7	Site 8	Site 9	Site 10	Site 10 duplicate	Site 11	Site 12	Site 12 Spike	Site 13	Site 14	Pigeon Bay	Offshore	Literature range (ng/L)	Reference
mParaben	April	<0.8	<0.8	65.7%	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	0.8	<0.8	<0.8	1.2	61.9%	0.9	NS	<0.8	1.1	5.1 – 21	[50]
	July	<0.8	<0.8	67.1%	–	<0.8	<0.8	<0.8	2.7	<0.8	<0.8	<0.8	<0.8	1.3	<0.8	<0.8	72.5%	<0.8	NS	<0.8	NS		
	October	<0.8	1.0	132.1%	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	1.0	1.5	<0.8	<0.8	135.9%	<0.8	NS	0.9	NS		
	January	–	–	85.5%	–	1.3	–	9.4	1.5	1.1	1.2	<0.8	0.9	1.1	1.0	1.0	97.8%	1.2	1.1	1.8	NS		
eParaben	April	–	–	60.9%	–	–	–	–	–	–	–	–	–	–	–	–	62.3%	–	NS	–	–		
	July	–	–	60.1%	–	–	–	–	–	–	–	–	–	–	–	–	66.3%	–	NS	–	NS		
	October	–	–	119.3%	–	–	–	–	–	–	–	–	–	–	–	–	120.5%	–	NS	–	NS		
	January	–	–	84.3%	–	–	–	–	–	–	–	–	–	–	–	–	96.7%	–	–	–	NS		
OP	April	–	0.4	62.1%	–	–	–	0.4	–	–	–	0.5	–	–	–	–	63.7%	–	NS	–	–	0.04 – 81	[77-79]
	July	–	–	68.9%	–	–	–	–	–	–	–	–	–	–	–	–	75.5%	–	NS	–	NS		
	October	0.4	–	168.6%	–	–	–	–	–	–	–	0.8	–	–	–	0.3	178.3%	–	NS	–	NS		
	January	–	–	80.8%	–	–	–	–	0.8	–	–	–	0.6	–	–	–	97.6%	–	–	–	NS		
pParaben	April	–	–	81.1%	–	–	–	–	–	–	–	–	–	–	–	–	81.3%	–	NS	–	–		
	July	–	–	83.6%	–	–	–	–	1.7	–	–	–	–	–	–	–	91.0%	–	NS	–	NS		
	October	–	–	112.4%	–	–	–	–	–	–	–	–	–	–	–	–	99.8%	–	NS	–	NS		
	January	–	<0.8	86.7%	–	–	–	2.2	1.0	–	–	<0.8	<0.8	<0.8	–	–	97.2%	–	–	–	NS		
bParaben	April	–	–	65.7%	–	–	–	0.8	–	–	–	–	–	<0.5	–	–	68.9%	–	NS	–	–	<0.2 –	[50]
	July	–	–	75.3%	–	–	–	–	0.9	–	–	–	–	–	–	–	80.9%	–	NS	–	NS	0.7	
	October	–	–	98.9%	–	–	–	–	–	–	–	–	–	–	–	–	85.0%	–	NS	–	NS		
	January	–	–	92.9%	–	–	–	–	–	–	–	–	–	–	–	–	103.7%	–	–	–	NS		
NP	April	–	–	52.2%	–	–	–	–	–	–	–	–	–	–	–	–	57.6%	–	NS	–	–		
	July	–	–	59.6%	–	–	–	–	–	–	–	–	–	–	–	–	69.8%	–	NS	–	NS		
	October	–	–	53.5%	–	–	–	–	–	–	–	–	–	–	–	–	68.0%	–	NS	–	NS		
	January	–	–	61.3%	–	–	–	–	–	–	–	–	–	–	–	–	63.7%	–	–	–	NS		
4-MBC	April	–	–	110.9%	–	–	–	–	–	5.1	–	–	–	–	–	–	115.3%	–	–	–	–	13.1 –	[39, 70]
	July	<3.2	<3.2	131.8%	–	<3.2	3.4	–	–	–	–	–	–	–	–	–	140.0%	–	–	–	NS	798.7	
	October	3.4	<3.2	124.4%	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	128.8%	<3.2	–	<3.2	NS		
	January	<3.2	<3.2	125.0%	<3.2	<3.2	<3.2	6.4	6.2	<3.2	<3.2	<3.2	6.5	<3.2	<3.2	<3.2	112.8%	<3.2	<3.2	–	NS		
BP-3	April	7.3	–	72.6%	<2.6	–	–	–	–	<2.6	–	–	–	<2.6	–	–	79.3%	5.1	–	–	<2.6	1.8 –	[71],
	July	<2.6	<2.6	113.1%	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	3.7	<2.6	119.3%	<2.6	–	<2.6	NS	3300	[38], [70]
	October	3.2	<2.6	149.9%	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	147.5%	<2.6	–	2.8	NS		
	January	<2.6	<2.6	123.7%	6.3	3.2	<2.6	3.0	6.2	<2.6	<2.6	<2.6	3.9	<2.6	<2.6	<2.6	114.1%	<2.6	<2.6	<2.6	NS		
mTric	April	–	–	74.5%	–	–	–	–	–	–	–	–	–	–	–	–	76.0%	–	NS	–	–		

	July	–	–	93.3%	–	–	–	–	–	–	–	–	–	–	–	102.0%	–	NS	–	NS		
	October	–	–	120.8%	–	–	–	–	–	–	–	–	–	–	–	125.3%	–	NS	–	NS		
	January	–	–	97.5%	–	–	–	–	–	–	–	–	–	–	–	101.5%	–	–	–	NS		
Triclosan	April	–	–	74.5%	–	–	–	–	–	–	–	–	–	–	–	74.7%	–	NS	–	–		
	July	–	–	90.9%	–	–	–	–	–	–	–	–	–	–	–	98.2%	–	NS	–	NS		
	October	–	–	131.8%	–	–	–	–	–	–	–	–	–	–	–	138.9%	–	NS	–	NS		
	January	–	–	123.9%	–	–	–	–	–	–	–	–	–	–	–	130.2%	–	–	–	NS		
BP-1	April	–	–	91.9%	–	–	–	–	3.3	–	–	–	–	–	–	91.6%	–	NS	1.3	–	280	[71]
	July	–	–	121.3%	–	–	–	–	–	–	–	–	–	–	–	132.2%	–	NS	–	NS		
	October	–	–	127.6%	–	–	–	–	–	–	–	–	–	–	–	125.4%	–	NS	–	NS		
	January	–	–	116.2%	–	–	–	–	–	–	–	<0.8	–	–	–	118.4%	–	–	–	NS		
BPA	April	<1.3	2.2	61.9%	<1.3	1.5	1.9	<1.3	2.0	<1.3	<1.3	4.9	<1.3	<1.3	<1.3	64.1%	1.4	NS	<1.3	2.9	0.11 –	[50], [77]
	July	2.6	3.1	88.5%	5.2	2.1	2.9	3.2	2.6	1.3	<1.3	2.9	3.1	4.7	1.9	5.0	91.0%	2.6	NS	<1.3	NS	5.7	
	October	–	–	87.8%	–	–	–	–	–	–	–	–	<1.3	–	1.3	2.9	80.4%	–	NS	–	NS		
	January	–	–	83.4%	–	–	–	–	–	–	–	–	2.2	–	–	–	97.1%	–	–	1.7	NS		
OMC	April	3.0	<1.9	87.7%	2.4	<1.9	–	<1.9	–	5.5	4.8	–	–	2.8	–	<1.9	84.7%	6.7	NS	–	3.2	7.4 –	[70]
	July	4.5	–	108.8%	4.0	–	–	<1.9	<1.9	<1.9	<1.9	<1.9	–	–	3.1	<1.9	117.6%	<1.9	NS	<1.9	NS	10.7	
	October	2.6	<1.9	56.2%	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	68.7%	<1.9	NS	<1.9	NS		
	January	4.1	<1.9	76.0%	4.0	3.7	<1.9	3.5	3.7	<1.9	<1.9	<1.9	4.1	<1.9	<1.9	<1.9	77.0%	<1.9	<1.9	–	NS		
E1	April	–	–	256.3%	–	–	–	–	<7.0	<7.0	<7.0	<7.0	–	–	–	–	263.6%	–	NS	–	–	0.08 – 85	[77]
	July	–	–	187.4%	–	–	–	–	–	–	–	–	–	–	–	–	202.5%	–	NS	–	NS		[181]
	October	<7.0	<7.0	104.1%	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	102.8%	<7.0	NS	<7.0	NS		[179]
	January	<7.0	<7.0	113.7%	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	<7.0	115.7%	<7.0	<7.0	<7.0	NS		[82]
E2	April	–	–	111.4%	–	–	–	–	–	–	–	–	–	–	–	–	115.7%	–	NS	–	–		
	July	<0.4	–	83.5%	–	–	–	–	–	–	–	–	–	–	–	<0.4	90.9%	–	NS	–	NS		
	October	–	–	89.8%	–	–	–	–	–	–	–	–	–	–	–	–	86.8%	–	NS	–	NS		
	January	–	–	88.9%	–	<0.4	<0.4	<0.4	<0.4	–	–	–	–	–	–	–	88.9%	–	<0.4	–	NS		
EE2	April	–	–	196.5%	–	–	–	–	–	–	–	–	–	–	–	–	200.9%	–	NS	–	–		
	July	–	–	128.1%	–	–	–	–	–	–	–	–	–	–	–	–	137.0%	–	NS	–	NS		
	October	–	–	100.7%	–	–	–	–	–	–	–	–	–	–	–	–	98.7	–	NS	–	NS		
	January	–	–	98.2%	–	–	–	–	–	–	–	–	–	–	–	–	103.2%	–	–	–	NS		
E3	April	–	–	120.4%	–	–	–	–	–	–	–	–	–	–	–	–	123.3%	–	NS	–	–		
	July	–	–	115.1%	–	–	–	–	–	–	–	–	–	–	–	<2.1	121.7%	–	NS	–	NS		
	October	–	–	96.6%	–	–	–	–	–	–	–	–	–	–	–	–	93.3%	–	NS	–	NS		
	January	–	–	84.8%	–	–	–	–	–	–	–	–	–	–	–	–	92.6%	–	–	–	NS		
Cstanol	April	–	–	103.7%	–	–	–	–	–	–	–	–	–	–	–	–	112.4%	–	NS	–	–		
	July	–	–	92.6%	–	–	5.4	–	–	–	2.4	2.8	–	–	–	–	106.3%	–	NS	–	NS		
	October	–	–		–	–	–	–	–	–	–	6.8	–	–	–	0.4		–	NS	–	NS		
	January	–	–		–	–	–	–	–	–	–	–	–	–	–	–		–	–	–	NS		

Table 8.6: Surrogate spike recoveries and statistical summary of Whakaraupo Harbour and Pigeon Bay seawater samples from the April, July, October, and January sampling rounds.

Analyte	Month	Site 1	Site 2	Site 2 Spike	Site 3	Site 4	Site 5	Site 6	Site 6 duplicate	Site 7	Site 8	Site 9
mParaben (ring $^{13}C_6$)	April	72.1%	73.6%	67.4%	73.6%	70.7%	68.0%	70.0%	63.0%	73.3%	66.8%	70.7%
	July	57.5%	60.4%	62.2%	57.8%	56.7%	56.0%	60.7%	66.3%	58.8%	60.9%	58.8%
	October	138.6%	134.1%	137.5%	138.1%	149.2%	138.8%	141.2%	146.4%	146.1%	144.0%	135.9%
	January	110.2%	112.4%	86.4%	111.0%	101.0%	102.5%	100.6%	104.0%	1088%	104.9%	101.2%
bParaben (ring $^{13}C_6$)	April	81.0%	78.2%	75.1%	80.1%	76.3%	76.7%	79.5%	74.7%	78.8%	78.2%	76.4%
	July	75.9%	74.7%	75.1%	72.8%	70.9%	72.5%	76.2%	81.2%	75.5%	76.1%	73.4%
	October	88.3%	88.2%	92.4%	91.3%	86.2%	90.0%	90.2%	99.5%	86.5%	83.9%	89.0%
	January	104.1%	98.1%	86.1%	100.4%	96.0%	102.3%	96.0%	96.9%	96.1%	94.9%	99.5%
NP (ring $^{13}C_6$)	April	44.5%	44.5%	41.9%	41.5%	44.3%	48.3%	48.4%	42.7%	45.6%	46.2%	45.4%
	July	49.6%	46.7%	46.0%	48.2%	50.9%	53.8%	58.0%	63.7%	57.6%	51.1%	54.6%
	October	61.5%	50.1%	52.6%	57.6%	61.0%	55.5%	60.3%	63.1%	58.6%	66.8%	60.3%
	January	75.8%	73.3%	69.4%	83.0%	75.0%	67.7%	69.7%	69.1%	68.8%	71.0%	72.3%
Tric (ring $^{13}C_{12}$)	April	78.6%	75.9%	75.6%	75.7%	74.5%	73.9%	78.6%	75.8%	75.5%	75.5%	74.2%
	July	89.3%	87.3%	91.6%	85.9%	83.2%	90.3%	85.9%	90.5%	88.0%	86.9%	89.1%
	October	132.9%	127.9%	132.5%	137.1%	141.1%	134.5%	136.3%	132.7%	141.5%	142.1%	131.4%
	January	138.7%	130.9%	123.7%	137.0%	126.8%	126.5%	134.0%	130.9%	129.8%	128.0%	139.6%
BPA (ring $^{13}C_{12}$)	April	66.3%	65.5%	66.7%	65.1%	66.5%	60.0%	66.9%	68.1%	65.4%	66.1%	65.2%
	July	83.9%	86.8%	86.9%	85.1%	84.7%	88.0%	85.7%	86.8%	86.0%	84.0%	86.6%
	October	88.9%	91.3%	92.7%	105.9%	88.6%	76.7%	95.1%	101.5%	91.5%	91.7%	72.3%
	January	73.2%	85.1%	85.2%	73.4%	81.0%	60.5%	81.7%	84.5%	77.0%	80.1%	72.6%
E2 (ring $^{13}C_6$)	April	109.0%	104.3%	102.5%	109.2%	104.1%	104.7%	109.9%	105.0%	107.3%	107.8%	105.6%
	July	69.9%	68.8%	73.0%	67.2%	72.6%	73.5%	78.7%	81.1%	70.1%	77.2%	73.9%
	October	81.8%	83.5%	87.4%	83.2%	86.8%	84.6%	84.2%	87.1%	87.0%	87.3%	85.6%
	January	91.4%	89.8%	92.9%	92.3%	88.5%	91.2%	92.7%	90.8%	89.9%	87.1%	94.9%

Table 8.6 continued: Surrogate spike recoveries and statistical summary of Whakaraupo Harbour and Pigeon Bay seawater samples from the April, July, October, and January sampling rounds.

Analyte	Site 10	Site 10 duplicate	Site 11	Site 12	Site 12 Spike	Site 13	Site 14	Pigeon Bay	Average	Std dev	%RSD	95% CI
mParaben (ring $^{13}C_6$)	70.0%	65.6%	65.4%	69.9%	64.9%	68.4%		63.7%	92.9%	31.8%	34.3%	7.9%
	47.3%	62.1%	61.5%	63.1%	68.1%	61.4%		55.7%				
	135.9%	143.9%	143.9%	122.5%	137.8%	129.5%		132.7%				
	95.2%	106.6%	95.4%	98.1%	93.8%	109.4%	105.8%	102.4%				
bParaben (ring $^{13}C_6$)	76.7%	76.0%	73.9%	77.2%	75.9%	76.5%		74.0%	85.0%	10.0%	11.7%	2.5%
	65.9%	77.3%	78.2%	77.6%	82.4%	75.7%		70.5%				
	95.0%	97.7%	96.0%	87.9%	80.4%	90.1%		89.4%				
	91.2%	98.3%	93.1%	92.0%	87.4%	97.6%	97.5%	94.5%				
NP (ring $^{13}C_6$)	45.0%	45.1%	43.9%	43.4%	48.0%	47.4%		46.6%	57.9%	10.5%	18.1%	2.6%
	47.5%	56.5%	56.4%	56.5%	57.0%	53.6%		52.7%				
	63.6%	59.1%	68.5%	64.9%	66.5%	60.5%		60.6%				
	73.5%	69.3%	65.9%	71.3%	69.3%	71.0%	69.8%	66.2%				
Tric (ring $^{13}C_{12}$)	74.6%	75.0%	73.6%	75.3%	76.4%	74.5%		74.6%	107.0%	26.0%	24.3%	6.4%
	85.5%	87.9%	89.1%	87.7%	97.9%	87.4%		87.0%				
	128.8%	131.4%	133.1%	118.0%	137.9%	123.2%		128.2%				
	133.9%	130.9%	126.6%	129.0%	125.2%	128.6%	130.9%	125.0%				
BPA (ring $^{13}C_{12}$)	66.8%	67.1%	65.4%	67.1%	67.8%	66.7%		64.3%	79.6%	11.2%	14.0%	2.8%
	79.4%	83.5%	85.0%	80.4%	87.4%	88.8%		86.3%				
	72.6%	95.1%	94.9%	80.0%	87.5%	65.1%		92.1%				
	96.8%	81.9%	74.7%	95.9%	94.3%	91.4%	72.0%	77.6%				
E2 (ring $^{13}C_6$)	108.5%	102.9%	104.2%	106.0%	107.2%	105.0%		103.1%	88.6%	12.6%	14.2%	3.1%
	63.7%	72.7%	74.7%	66.6%	79.9%	77.7%		69.5%				
	83.0%	87.3%	84.2%	75.2%	86.0%	82.9%		84.6%				
	96.2%	92.3%	91.1%	91.1%	93.1%	94.0%	92.9%	90.4%				

Table 8.7: Analytes concentrations (ng g^{-1} dry weight) and analyte spike recoveries in marine sediments from Whakaraupo Harbour and Pigeon Bay collected in April and October 2012, and a North Island reference site.

Analyte	Month	Site 1	Site 2	Site 3	Site 4	Site 5	Site 5 duplicate	Site 6	Site 7	Site 7 duplicate	Site 8	Site 9	Site 9 duplicate	Site 10	Site 11	Site 12	Site 13	Site 13 Spike	Pigeon Bay	Reference Site (± std.dev, n=7)
mParaben	April	–	–	–	–	–	–	–	–	–	–	1.7	0.7	–	–	0.9	–	112.7%	–	0.9 ± 0.3
	October	0.3	0.3	0.2	0.2	0.4	NA	–	–	<0.2	0.4	0.4	0.4	–	0.3	<0.2	0.4	76.5%	0.7	
eParaben	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	137.2%	–	
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	78.8%	–	
OP	April	0.8	0.2	0.6	1.0	0.6	1.0	2.5	1.5	0.3	–	1.2	1.0	0.3	0.7	1.5	1.8	79.3%	–	1.0 ± 0.5
	October	–	–	–	–	–	NA	–	–	–	–	0.5	0.6	–	–	0.6	–	91.3%	–	
pParaben	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	134.0%	–	
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	74.0%	–	
bParaben	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	127.0%	–	
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	81.7%	–	
NP	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	76.6%	–	
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	78.9%	–	
4-MBC	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	178.1%	–	
	October	–	–	–	–	2.0	NA	–	–	–	–	–	–	–	4.3	1.8	4.5	52.0%	1.6	
BP-3	April	<0.8	<0.8	0.8	0.9	0.8	0.5	1.2	0.8	<0.8	<0.8	1.6	1.2	–	1.2	–	–	121.4%	–	2.5 ± 0.3
	October	–	–	–	–	–	NA	–	–	–	<0.8	<0.8	<0.8	–	–	–	–	115.4%	<0.8	
mTric	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	82.6%	–	
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	77.5%	–	
Triclosan	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	88.0%	–	
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	114.%	–	
BP-1	April	–	1.3	0.9	1.0	0.5	0.4	0.5	0.4	–	–	–	–	–	–	–	–	102.1%	–	1.3 ± 0.4
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	104.5%	–	
BPA	April	–	<0.4	0.4	0.7	<0.4	0.5	0.5	<0.4	–	<0.4	7.1	4.6	<0.4	<0.4	<0.4	<0.4	105.4%	–	
	October	–	–	–	–	–	NA	–	–	–	–	9.9	1.8	–	–	–	–	68.4%	–	
OMC	April	1.1	0.9	1.3	2.8	1.0	1.2	2.6	1.5	0.8	–	–	–	–	–	–	–	88.8%	–	1.4 ± 0.6
	October	–	–	–	–	1.2	NA	–	–	0.9	2.6	<0.6	–	<0.6	5.6	1.9	11.5	–	3.8	
E1	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	70.4%	–	5.1 ± 1.1
	October	<2.0	<2.0	<2.0	<2.0	<2.0	NA	<2.0	<2.0	<2.0	<2.0	<2.0	–	<2.0	<2.0	<2.0	<2.0	111.0%	–	
E2	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	99.3%	–	
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	88.3%	–	
EE2	April	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	110.1%	–	
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	131.6%	–	
E3	April	–	0.6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	104.2%	–	
	October	–	–	–	–	–	NA	–	–	–	–	–	–	–	–	–	–	82.8%	–	
Cstanol	April	8.6	7.1	7.0	13.5	2.6	4.8	15.8	11.0	14.5	6.4	14.1	16.7	4.3	13.3	6.7	18.7	NA	13.5	17.4 ± 2.1
	October	2.0	3.3	8.1	4.0	5.4	NA	6.6	11.4	7.3	6.8	73.1	98.7	3.2	7.7	3.5	8.4	90.2%	21.3	
Cstan-3-one	April	13.5	13.4	12.6	17.8	6.5	9.0	23.6	19.5	24.2	16.8	16.7	15.9	7.7	24.4	15.5	24.7	NA	18.5	15.6 ± 0.7
	October	7.0	12.8	32.2	24.3	74.0	NA	33.7	36.6	25.4	43.8	91.7	131.4	11.3	26.7	13.0	24.0	171.2%	48.7	

Table 8.8: Surrogate spike recoveries and statistical summary of the marine sediment samples from Whakaraupo Harbour and Pigeon Bay collected in April and October 2012.

Surrogate	Month	Site 1	Site 2	Site 3	Site 4	Site 5	Site 5 duplicate	Site 6	Site 7	Site 7 duplicate	Site 8	Site 9	Site 9 duplicate
mParaben (ring $^{13}C_6$)	April	106.6%	110.0%	116.1%	107.2%	96.5%	85.8%	88.1%	89.0%	125.7%	117.6%	138.7%	133.3%
	October	89.1%	43.2%	84.5%	52.7%	79.4%	NA	84.7%	26.7%	76.2%	56.3%	77.5%	48.4%
bParaben (ring $^{13}C_6$)	April	101.2%	92.2%	114.0%	97.4%	92.4%	80.1%	87.3%	85.5%	116.1%	108.6%	113.5%	108.3%
	October	77.1%	34.7%	69.4%	48.2%	70.6%	NA	72.0%	26.8%	71.9%	55.5%	73.6%	59.6%
NP (ring $^{13}C_6$)	April	107.5%	106.2%	116.3%	113.9%	83.4%	103.1%	109.6%	97.2%	94.8%	75.3%	105.3%	89.6%
	October	54.4%	30.9%	66.5%	37.8%	51.8%	NA	61.4%	64.5%	88.8%	66.4%	76.1%	81.2%
Tric (ring $^{13}C_{12}$)	April	68.6%	73.0%	85.0%	81.7%	59.1%	80.5%	84.4%	81.7%	99.3%	87.6%	108.3%	95.2%
	October	102.0%	56.5%	97.7%	59.5%	78.1%	NA	104.0%	87.4%	102.9%	88.5%	94.7%	92.6%
BPA (ring $^{13}C_{12}$)	April	46.8%	106.1%	83.6%	92.0%	86.7%	94.5%	98.1%	82.3%	98.4%	90.2%	86.7%	70.0%
	October	84.7%	33.7%	86.0%	63.0%	84.8%	NA	90.1%	67.7%	82.7%	71.6%	81.4%	72.1%
E2 (ring $^{13}C_6$)	April	81.3%	80.3%	65.9%	75.5%	75.1%	69.3%	71.1%	68.2%	73.3%	66.8%	61.1%	50.5%
	October	81.5%	43.5%	84.0%	59.8%	84.5%	NA	84.1%	68.2%	85.9%	79.0%	84.4%	79.1%

Table 8.8 continued: Surrogate spike recoveries and statistical summary of the marine sediment samples from Whakaraupo Harbour and Pigeon Bay collected in April and October 2012.

Surrogate	Site 10	Site 11	Site 12	Site 13	Site 13 Spike	Pigeon Bay	Average	Std dev	%RSD	95% C.I. (n=35)
mParaben (ring $^{13}C_6$)	95.5%	138.7%	116.4%	117.8%	117.6%	57.1%	87.4%	29.5%	33.8%	10.1%
	66.4%	86.1%	68.4%	49.1%	68.7%	44.8%				
bParaben (ring $^{13}C_6$)	85.8%	124.0%	102.6%	109.9%	96.7%	53.8%	79.6%	24.8%	31.2%	8.5%
	57.7%	76.2%	60.1%	49.1%	58.6%	53.4%				
NP (ring $^{13}C_6$)	74.2%	111.1%	83.9%	108.7%	87.8%	64.7%	83.3%	21.4%	25.6%	7.3%
	72.7%	97.9%	77.7%	85.2%	86.0%	82.6%				
Tric (ring $^{13}C_{12}$)	84.0%	98.8%	91.7%	105.1%	98.3%	61.2%	88.4%	14.6%	16.5%	5.0%
	88.3%	107.8%	87.6%	100.9%	109.6%	91.1%				
BPA (ring $^{13}C_{12}$)	81.1%	98.1%	94.7%	107.5%	111.2%	61.3%	81.9%	16.1%	19.7%	5.5%
	71.8%	85.3%	66.6%	84.1%	74.8%	76.5%				
E2 (ring $^{13}C_6$)	62.0%	80.7%	68.7%	79.4%	75.0%	48.6	73.9%	11.5%	15.6%	4.0%
	73.2%	92.1%	79.4%	85.2%	89.4%	80.4%%				

Table 8.9: Dry weight percentages of marine sediments from Whakaraupo Harbour collected in April 2012 and October 2012.

Month	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Pigeon Bay	Reference Site
April	75.2%	73.8%	67.5%	54.7%	74.2%	62.7%	72.3%	72.5%	61.1%	72.8%	60.7%	64.7%	60.9%	68.7%	58.8%
	73.8%	73.9%	67.5%	54.8%	74.6%	63.2%	72.4%	72.1%	61.0%	74.3%	60.7%	65.2%	59.5%	68.7%	59.9%
October	73.1%	74.4%	64.0%	68.4%	68.1%	65.5%	72.7%	67.4%	52.4%	74.2%	64.6%	65.9%	65.0%	57.7%	NA
	75.2%	74,6%	62.7%	67.5%	68.8%	65.1%	72.9%	66.5%	53.2%	74.4%	64.0%	63.0%	65.4%	58.4%	

Table 8.10: Dry weight percentages and composite data of the New Zealand green lipped mussel composites of Sandy Bay, Rapaki, Battery Point, Port Levy, and Pigeon Bay from April 2012 and January 2013.

	April 2012					January 2013			
	Sandy Bay	Rapaki	Port Levy	Pigeon Bay	Battery Point	Sandy Bay	Port Levy	Pigeon Bay	Battery Point
Sampling date	06/04/2012	06/04/2012	10/04/2012	10/04/2012	19/04/2012	29/01/2013	29/01/2013	25//01/2013	25/01/2013
Dry weight percentage	24.0%	21.8%	22.2%	22.5%	19.0%	17.5%	19.4%	19.9%	19.4%
	24.2%	21.2%	22.1%	22.3%	19.4%	18.6%	19.3%	20.3%	19.5%
Lipid percentage (dry weights)	1.3%	1.5%	1.1%	2.3%	0.9%	0.6%	0.8%	1.5%	0.8%
Mussel tissue weight used (g)	17.83	12.44	19.03	16.25	11.90	11.88	9.18	13.59	12.93
	17.43	9.85	14.14	17.27	17.94	11.05	9.90	21.67	15.55
	12.72	12.03	15.57	16.93	14.07	9.50	10.70	22.94	13.84
	10.66	10.29	18.72	19.34	21.14	13.45	13.93	24.00	18.07
	10.92	9.51	14.95	18.14	17.97	8.73	12.31	19.37	22.45
	11.33	22.77	19.65	41.86	18.07	13.08	12.78	18.86	19.60
	16.30	21.26	24.24	36.35	18.41	15.62	13.10	27.14	22.53
	20.49	43.02	21.80	41.14	30.94	15.27	13.10	22.76	19.40

Table 8.11: Analyte concentrations (ng g^{-1} dry weight) and surrogate & analyte spike recoveries from the New Zealand green lipped mussel composites of April 2012 and January 2013.

	April 2012					January 2013				
Analyte	Sandy Bay	Rapaki	Port Levy	Pigeon Bay	Battery Point	Sandy Bay	Port Levy	Pigeon Bay	Battery Point	Pigeon Bay Spike
mParaben	16.9	15.8	14.2	5.0	21.3	14.0	5.6	5.6	4.6	94.3%
eParaben										78.0%
OP	3.8	8.8	ND	ND	8.9	6.5	2.7	4.0	4.5	99.8%
pParaben										112.2%
bParaben										26.8%
NP										NR
4-MBC										NR
BP-3	ND	ND	ND	ND	ND	ND	19.1	ND	ND	95.6%
mTric										NR
Triclosan										NR
BP-1										NR
BPA										NR
OMC										NR
E1										NR
E2										66.6%
EE2										82.6%
E3										58.1%
Cstanol										
mParaben (ring $^{13}C_6$)	185.1%	125.8%	116.1%	110.3%	93.7%	95.3%	94.7%	121.9%	91.8%	92.8%
bParaben (ring $^{13}C_6$)	163.7%	122.5%	NR	95.4%	96.4%	88.4%	89.5%	119.6%	94.8%	87.1%
NP (ring $^{13}C_6$)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Tric (ring $^{13}C_{12}$)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
BPA (ring $^{13}C_{12}$)	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
E2 (ring $^{13}C_6$)	81.2%	68.2%	59.7%	69.4%	81.2%	83.0%	82.6%	75.5%	86.9%	60.0%

NR = not recovered

9 Appendix B

Table 9.1: Isotope labelled surrogate recoveries and statistics summary of the 2009/2010 research season sewage effluent samples.

Isotope Surrogate	SB 24 Oct 2009	SB duplicate 24 Oct 2009	McM 28 Oct 2009	McM duplicate 28 Oct 2009	Average % Recovery	Std dev	%RSD	95% C.I.
mParaben (ring $^{13}C_6$)	83.9%	81.9%	119.2%	125.7%	102.7%	23.0%	22.4%	36.6%
bParaben (ring $^{13}C_6$)	98.7%	97.4%	128.1%	131.8%	114.0%	18.5%	16.2%	29.4%
NP (ring $^{13}C_6$)	N/Q	N/Q	90.7%	79.2%	84.9%	8.1%	9.6%	72.9%
BPA (ring $^{13}C_{12}$)	95.1%	60.9%	105.0%	111.0%	93.0%	22.4%	24.1%	35.6%

SB = Scott Base, McM = McMurdo Station, N/Q = peak not quantifiable

Table 9.2a: Isotope labelled surrogate recoveries of the 2009/2010 research season Antarctic seawater samples.

Analyte	CA	CA duplicate	WQB 1	WQB 1 duplicate	WQB 2	WQB 3	C-SB 1	C-SB 1 duplicate	C-SB 2	C-SB 3	C-SB 4	C-SB 5	C-SB 5 duplicate	CE	CE duplicate
mParaben (ring $^{13}C_6$)	69.4%	84.7%	72.5%	66.5%	76.4%	98.6%	85.4%	95.1%	91.8%	97.6%	96.2%	95.0%	83.7%	85.95%	101.3%
bParaben (ring $^{13}C_6$)	76.4%	87.2%	85.7%	75.7%	89.3%	94.3%	87.4%	95.4%	97.6%	101.8%	97.5%	99.8%	90.3%	99.10%	105.2%
NP (ring $^{13}C_6$)	56.9%	49.9%	62.6%	40.8%	49.3%	59.0%	57.8%	56.1%	61.8%	62.5%	62.3%	71.2%	67.5%	66.95%	70.4%
BPA (ring $^{13}C_{12}$)	97.7%	110.0%	107.0%	97.1%	102.0%	95.4%	112.3%	113.7%	104.0%	115.5%	113.8%	113.1%	97.2%	51.46%	83.9%

CA = Cape Armitage, WQB = Winter Quarters Bay, C-SB = coastal area off Scott Base, CE = Cape Evans

Table 9.2b: Statistics summary of the surrogate recoveries of the 2009/2010 research season seawater samples (excluding the 10 L samples from CE).

Isotope Surrogate	Average % Recovery (n = 13)	Std dev	%RSD	95% C.I.
mParaben (ring $^{13}C_6$)	85.6%	11.3%	13.2%	6.8%
bParaben (ring $^{13}C_6$)	90.6%	8.2%	9.1%	5.0%
NP (ring $^{13}C_6$)	58.3%	8.1%	13.8%	4.9%
BPA (ring $^{13}C_{12}$)	106.1%	7.5%	7.1%	4.5%

Table 9.3: Laboratory background concentrations (ng L^{-1}) of target analytes in the comparative standards and MQ blanks prepared in parallel to the environmental samples during the 2009/2010 research season.

Analyte	CA/WQB 1 comparative standard	WQB 2+3 comparative standard	C-SB comparative standard	CE comparative standard	SB sewage comparative standard	McM sewage comparative standard	MQ Blank 1 comparative standard	MQ Blank 2 comparative standard	MQ Blank 1	MQ Blank 2
mParaben	3.2	3.7	3.8	–	2.9	2.9	2.7	3.6	1.3	1.7
OP	1.0	0.7	0.5	0.2	0.8	0.5	0.5	0.5	1.1	4.5
BP-3	4.9	1.1	11.9	1.5	1.7	0.8	0.8	7.8	15.7	36.7
Triclosan	–	–	–	–	–	–	–	–	–	0.3
BP-1	0.1	0.1	0.6	0.6	–	0.1	0.1	0.5	–	1.8
BPA	4.3	–	–	7.3	–	–	–	–	4.9	–
OMC	–	–	–	0.5	–	–	–	–	–	–

Table 9.4: Concentrations (ng L^{-1}) of detected target analytes in 2009/2010 Scott Base and McMurdo sewage effluent samples.

Analyte	SB 24 Oct 2009	SB duplicate 24 Oct 2009	McM 28 Oct 2009	McM duplicate 28 Oct 2009
mParaben	–	–	–	–
eParaben	–	–	–	–
OP	101.1	118.0	–	–
pParaben	–	–	–	–
bParaben	–	–	–	–
3PBOH	–	–	–	–
NP	–	–	–	–
4-MBC	173.0	216.8	–	–
BP-3	89.7	70.0	130.7	110.5
mTric	–	–	–	–
Tric	225.9	248.5	–	–
BP-1	143.1	170.7	7.2	7.3
BPA	31.9	22.9	28.0	28.0
OMC	–	–	–	–
E1	40.9	45.7	–	–

E2	–	–	–	–
Cstane	–	–	–	–
EE2	–	–	–	–
E3	–	–	–	–
Cstanol	–	–	–	–
Cstan-3-one	–	–	–	–

SB = Scott Base, McM = McMurdo Station

Table 9.5: Concentrations (ng L^{-1}) of detected target analytes in Antarctic seawater during the 2009/2010 research season.

Analyte	CA	CA duplicate	WQB 1	WQB 1 duplicate	WQB 2	WQB 3	C-SB 1*	C-SB 1 duplicate*	C-SB 2*	C-SB 3*	C-SB 4*	C-SB 5*	C-SB 5 duplicate*	CE	CE duplicate
mParaben	31.8	33.3	2.9	7.8	6.8	7.1	42.4	33.6	242.4	145.1	40.2	67.3	50.2	1.9	1.9
eParaben	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
OP	1.7	1.6	0.3	0.4	0.6	1.5	0.6	–	1.0	1.8	0.7	0.7	–	0.5	0.3
pParaben	<0.8**	<0.8**	–	–	3.0	–	9.5	7.1	57.8	55.1	10.4	23.7	19.5	1.6	1.5
bParaben	2.3	2.0	–	–	<0.5**	–	–	–	1.8	–	–	–	–	–	–
3PBOH	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
NP	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
4-MBC	47.5	42.7	–	–	–	–	–	–	–	–	–	–	–	–	–
BP-3	80.8	50.7	23.7	12.0	88.4	34.0	367.2	237.7	809.3	1236.8	458.2	775.8	643.4	28.9	29.9
mTric	–	–	–	–	–	–	–	–	–	–	–	–	–	<0.2	<0.2
Tric	0.6	0.8	0.5	<0.5	0.8	–	0.5	0.6	1.1	1.7	0.6	1.1	0.8	<0.5	<0.5
BP-1	10.3	6.3	–	–	<0.8**	–	1.3	1.4	2.2	2.6	1.4	1.5	1.3	–	–
BPA	29.5	31.1	6.1	6.6	11.0	6.6	2.7	2.6	8.8	8.5	2.5	3.7	4.3	2.2	3.0
OMC	32.3	41.7	<1.9**	8.5	18.6	6.0	3.6	5.1	10.8	10.1	2.7	6.2	7.2	2.9	3.8
E1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
E2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
EE2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
E3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

CA = Cape Armitage, WQB = Winter Quarters Bay, C-SB = coastal area off Scott Base, CE = Cape Evans
*Excluded from discussions due to likely contamination during sampling.
**Not quantifiable due to matrix effects.

Table 9.6: Surrogate recoveries of Scott Base effluent collected during the 2012/2013 research season.

Analyte	August	August	October	October	November	November	December	December	January*	January*	February*	February*	Average	Std dev	%RSD	95% C.I.
mParaben (ring $^{13}C_6$)	148.8%	139.7%	213.8%	178.7%	122.7%	136.7%	145.5%	135.6%	95.2%	112.5%	99.2%	109.0%	136.4%	33.9%	24.8%	21.5%
bParaben (ring $^{13}C_6$)	104.9%	108.9%	120.0%	130.8%	119.8%	124.7%	126.8%	128.5%	110.7%	119.4%	100.5%	97.0%	116.0%	11.3%	9.8%	7.2%
NP (ring $^{13}C_6$)	97.1%	134.0%	133.2%	110.1%	50.6%	20.6%	0%	0%	75.2%	88.1%	88.5%	38.9%	69.7%	47.4%	68.0%	30.1%
Tric (ring $^{13}C_{12}$)	136.1%	135.8%	179.2%	161.3%	114.3%	113.3%	117.3%	128.5%	123.6%	104.9%	126.0%	107.5%	129.0%	22.0%	17.1%	14.0%
BPA (ring $^{13}C_{12}$)	94.7%	89.6%	84.3%	88.5%	100.6%	95.6%	74.9%	73.0%	94.9%	91.7%	98.5%	90.6%	89.7%	8.6%	9.6%	5.5%
E2 (ring $^{13}C_6$)	85.5%	85.3%	80.4%	82.7%	72.2%	37.0%	73.6%	70.3%	83.3%	82.3%	73.8%	71.5%	74.9%	13.2%	17.6%	8.4%

*Ozonation plant in operation.

Table 9.7: Recoveries of the Scott Base effluent analyte and surrogate spike collected during the 2012/2013 research season.

Analyte	29th August	9th October	7th November	28th November	January**	February**
mParaben	118.7%	133.6%	122.5%	95.0%	108.3%	110.8%
eParaben	132.8%	142.0%	109.2%	95.3%	100.1%	101.1%
OP	243.1%*	129.3%	91.8%	30.0%	76.3%	89.3%
pParaben	134.6%	146.6%	136.5%	111.9%	92.8%	102.7%
bParaben	90.7%	92.7%	88.3%	115.3%	112.0%	112.9%
NP	81.0%	96.1%	64.9%	43.7%	65.6%	72.5%
4-MBC	103.7%	122.7%	92.3%	–*	–*	–*
BP-3	144.5%	177.2%	77.2%	119.8%	104.7%	112.0%
mTric	97.5%	89.1%	79.4%	120.5%	97.3%	111.1%
Tric	103.6%	103.1%	92.1%	78.3%	139.8%	111.6%
BP-1	135.5%	163.1%	71.3%	100.0%	101.1%	176.3%
BPA	88.4%	76.1%	86.9%	118.2%	79.2%	98.2%
OMC	94.0%	68.4%	73.2%	106.2%	96.3%	100.0%
E1	125.9%	94.9%	208.7%	66.8%	108.9%	109.1%
E2	61.2%	99.3%	97.4%	83.2%	81.7%	82.7%
EE2	108.1%	106.9%	117.0%	152.7%	90.7%	99.0%

E3	97.9%	115.4%	106.6%	95.2%	82.7%	91.7%
mParaben (ring $^{13}C_6$)	131.9%	165.4%	116.4%	176.9%	112.3%	124.7%
bParaben (ring $^{13}C_6$)	102.6%	120.1%	123.6%	135.3%	124.7%	102.8%
NP (ring $^{13}C_6$)	112.8%	90.9%	–	–	84.9%	86.5%
Tric (ring $^{13}C_{12}$)	129.3%	129.9%	111.9%	128.6%	77.2%	129.2%
BPA (ring $^{13}C_{12}$)	89.8%	79.3%	93.4%	68.4%	82.6%	97.7%
E2 (ring $^{13}C_6$)	56.9%	78.6%	77.8%	73.6%	89.9%	83.5%

*Recovery accuracy was affected by the presence of high concentrations of analyte.
**Ozonation plant in operation.

Table 9.8: Analytes detected in the Scott Base effluent collected over the 2012/2013 research season.

Analyte	August	August	October	October	November	November	December	December	January*	January*	February*	February*
mParaben	ND	ND	22.7	25.1	ND	ND	ND	ND	ND	ND	ND	ND
eParaben	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
OP	3824.2	4066.0	349.1	353.8	29.0	27.1	636.0	560.5	7.5	10.5	38.3	39.0
pParaben	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
bParaben	ND	ND	ND	ND	9.7	11.0	ND	ND	ND	ND	ND	ND
NP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-MBC	320.7	350.7	338.2	342.7	370.1	352.5	784.8	661.9	2021.4	2126.9	975.8	1048.0
BP-3	51.3	56.5	114.8	110.2	25.1	29.7	43.5	42.8	19.0	16.7	28.7	30.3
mTric	26.0	27.2	23.9	24.9	40.6	38.0	30.9	32.1	28.0	32.2	23.6	19.3
Tric	133.8	132.4	266.0	279.5	75.7	75.2	357.3	316.2	82.8	91.1	80.6	80.7
BP-1	47.1	48.0	177.1	177.7	55.8	54.4	461.1	417.7	26.0	24.3	124.1	122.3
BPA	50.9	45.8	50.7	56.0	9.2	10.0	97.3	82.0	4.7	8.6	14.8	15.7
OMC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
E1	13.3	13.5	11.2	12.0	3.1	3.6	17.7	21.8	ND	ND	ND	ND
E2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
EE2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
E3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cstanol	402.3	455.1	560.7	593.5	193.8	176.7	167.8	166.5	569.5	464.2	175.2	202.4

* Ozonation plant in operation
ND = not detected

Table 9.9: Analytes detected over the seven-day monitoring of Scott Base sewage effluent concentrations in December 2012.

Analyte	Dec 9th	Dec 9th	Dec 10th	Dec 10th	Dec 11th	Dec 11th	Dec 12th	Dec 12th	Dec 13th	Dec 13th	Dec 14th	Dec 14th	Dec 15th	Dec 15th
mParaben	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
eParaben	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
OP	1051.9	1003.8	928.6	946.1	2145.4	2277.3	3207.3	3071.7	7053.8	6993.4	2210.9	1946.0	5472.0	3600.8
pParaben	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
bParaben	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
NP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-MBC	4578.8	4482.9	3592.9	3623.5	4242.8	5204.5	4787.4	3738.8	11308.7	11725.9	5481.8	4771.0	4471.4	3253.6
BP-3	153.6	182.7	194.6	143.2	154.1	183.4	171.1	122.8	144.5	152.4	68.4	65.8	77.0	90.9
mTric	40.9	35.8	38.6	36.7	36.7	36.1	40.0	36.8	32.8	38.8	42.5	39.9	32.9	31.6
Tric	449.6	467.1	458.0	456.7	632.8	635.0	622.2	611.1	767.8	807.1	680.9	650.8	545.3	541.6
BP-1	2121.8	2323.5	2462.7	1818.9	2146.5	2341.8	6832.2	6633.9	2361.8	2404.1	273.3	264.8	6018.4	4690.2
BPA	286.0	308.6	481.5	494.1	707.5	763.3	985.7	963.8	625.7	614.9	508.4	459.5	887.8	746.3
OMC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
E1	137.3	145.0	107.9	107.3	113.4	108.8	228.9	218.4	331.6	326.6	149.1	139.3	188.0	217.2
E2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
EE2	13.8	11.5	20.3	22.0	44.6	48.6	68.1	77.8	43.6	41.6	55.7	47.1	75.1	70.1
E3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	47.6	41.4
Cstanol	1099.4	905.0	1362.6	838.4	869.1	1034.3	1060.3	874.1	1165.2	1389.4	1040.8	724.6	2697.3	1340.5

ND = not detected

Table 9.10: Surrogate recoveries and statistical summary of the three rounds of seawater samples collected during the 2012/2013 research season.

Surrogate	Round	Site 1	Site 1 Spike	Site 2	Site 2 duplicate	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14
mParaben (ring $^{13}C_6$)	Round 1	102.4%	100.8%	108.0%	116.5%	102.7%	103.9%	112.4%	109.8%	89.4%	110.8%	104.8%	103.9%	109.5%	124.5%	121.6%	112.7%
	Round 2	122.4%	102.1%	125.9%	127.8%	124.9%	125.6%	108.5%	136.7%	141.2%	136.6%	129.3%	127.7%	132.9%	126.5%	102.2%	126.4%
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
bParaben (ring $^{13}C_6$)	Round 1	88.5%	81.7%	84.1%	89.0%	81.0%	84.9%	85.3%	79.7%	76.8%	62.4%	48.2%	47.2%	67.0%	86.3%	95.9%	48.0%
	Round 2	85.2%	86.2%	84.2%	88.6%	84.3%	85.3%	80.9%	89.2%	93.3%	69.4%	80.8%	81.7%	70.0%	66.4%	73.4%	75.8%
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

NP (ring $^{13}C_6$)	Round 1	59.1%	57.8%	55.2%	62.2%	63.8%	50.2%	45.9%	43.6%	46.4%	31.2%	25.5%	19.2%	38.0%	38.2%	70.7%	21.6%
	Round 2	66.6%	71.2%	55.2%	72.2%	61.4%	46.1%	60.3%	43.7%	48.9%	38.4%	48.4%	43.8%	N/A	30.0%	51.3%	47.1%
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Tric (ring $^{13}C_{12}$)	Round 1	137.6%	139.4%	136.2%	137.0%	126.4%	128.7%	130.6%	132.7%	118.0%	127.2%	128.2%	132.6%	131.1%	136.5%	139.6%	132.0%
	Round 2	108.4%	103.0%	108.9%	108.9%	108.9%	111.5%	106.4%	107.6%	110.9%	107.5%	105.2%	99.8%	108.8%	99.8%	92.7%	104.5%
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
BPA (ring $^{13}C_{12}$)	Round 1	80.0%	84.1%	96.6%	97.5%	73.8%	80.3%	97.5%	96.9%	72.6%	85.7%	85.1%	83.8%	76.6%	92.7%	95.2%	84.5%
	Round 2	87.9%	68.2%	81.4%	92.4%	91.9%	81.9%	79.5%	84.0%	87.4%	94.6%	93.9%	80.3%	92.8%	83.1%	89.9%	79.8%
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
E2 (ring $^{13}C_6$)	Round 1	82.7%	92.0%	79.8%	94.1%	77.1%	70.8%	80.7%	76.8%	71.6%	83.2%	79.7%	80.6%	78.9%	85.1%	89.5%	85.8%
	Round 2	104.5%	103.0%	105.4%	109.6%	104.0%	80.5%	103.5%	77.6%	84.3%	108.1%	106.7%	99.7%	110.3%	99.3%	100.8%	105.8%
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

Table 9.10 continued: Surrogate recoveries and statistical summary of the three rounds of seawater samples collected during the 2012/2013 research season.

Surrogate	Round	Site 15	Site 15 duplicate	Site 16	Site 17	Site 18	Site 19	Site 20	Site 21	Site 22	Site 23	Site 23 Spike	Site 24	Site 24 duplicate	Site 24 Spike	Average	Std.dev.	%RSD	95% C.I.
mParaben (ring $^{13}C_6$)	Round 1	–	–	–	110.8%	–	–	–	89.3%	111.2%	105.7%	98.4%	108.8%	80.4%	–	109.4%	16.7%	15.2%	4.4%
	Round 2	–	–	–	122.9%	–	–	–	125.3%	N/A	128.4%	129.4%	119.5%	119.7%	–				
	Round 3	79.2%	93.2%	83.1%	94.2%	86.9%	93.4%	91.5%	83.9%	83.0%	80.2%	–	91.1%	–	94.1%				
bParaben (ring $^{13}C_6$)	Round 1	–	–	–	89.4%	–	–	–	76.8%	88.5%	87.4%	79.3%	90.0%	67.5%	–	78.9%	12.7%	16.1%	3.4%
	Round 2	–	–	–	82.7	–	–	–	83.8%	N/A	85.2%	88.5%	85.3%	83.7%	–				
	Round 3	47.9%	49.3%	71.8%	89.5%	85.0%	91.4%	49.8%	83.5%	79.7%	80.7%	–	88.7%	–	90.9%				
NP (ring $^{13}C_6$)	Round 1	–	–	–	74.9%	–	–	–	65.0%	74.8%	65.0%	62.8%	75.7%	50.1%	–	55.3%	16.2%	29.3%	4.3%
	Round 2	–	–	–	54.8%	–	–	–	54.2%	N/A	62.1%	65.2%	67.0%	65.0%	–				
	Round 3	28.5%	28.6%	53.6%	74.8%	64.5%	80.6%	35.8%	71.7%	67.9%	76.8%	–	81.1%	–	82.9%				
Tric (ring $^{13}C_{12}$)	Round 1	–	–	–	135.5%	–	–	–	124.7%	138.0%	135.8%	128.1%	142.0%	105.8%	–	116.7%	14.1%	12.1%	3.7%
	Round 2	–	–	–	99.8%	–	–	–	98.1%	N/A	100.8%	106.7%	98.4%	105.0%	–				
	Round 3	100.3%	109.1%	104.0%	116.6%	119.1%	113.4%	101.0%	109.1%	108.7%	106.5%	–	114.6%	–	118.2%				
BPA (ring $^{13}C_{12}$)	Round 1	–	–	–	74.3%	–	–	–	77.7%	78.7%	83.4%	92.6%	67.3%	76.9%	–	81.6%	10.0%	12.3%	2.7%
	Round 2	–	–	–	85.9%	–	–	–	83.2%	N/A	93.5%	92.8%	83.3%	53.3%	–				
	Round 3	58.1%	70.6%	69.9%	77.6%	74.8%	70.4%	65.2%	70.9%	68.2%	74.2%	–	78.3%	–	80.7%				
E2 (ring $^{13}C_6$)	Round 1	–	–	–	83.7%	–	–	–	83.3%	80.8%	79.5%	84.3%	89.4%	67.0%	–	84.9%	16.4%	19.3%	4.3%
	Round 2	–	–	–	103.3%	–	–	–	104.6%	N/A	101.4%	102.2%	101.8%	101.5%	–				
	Round 3	56.8%	61.2%	56.0%	70.1%	61.9%	67.4%	51.2%	65.6%	57.5%	62.1%	–	68.7%	–	65.3%				

Table 9.11: Surrogate recoveries and statistical summary of the five molten sea ice samples collected during sampling round 2 of the 2012/2013 research season.

Surrogate	Site 2	Site 7	Site 14	Site 17	Site 24	Average	Std. dev.	%RSD	95% C.I.
mParaben (ring $^{13}C_6$)	123.6%	144.8%	126.0%	124.5%	121.0%	126.6%	9.2%	7.3%	11.4%
bParaben (ring $^{13}C_6$)	83.4%	107.0%	82.6%	83.4%	81.6%	86.9%	9.9%	11.4%	12.3%
NP (ring $^{13}C_6$)	54.6%	69.9%	70.5%	83.8%	62.2%	67.7%	9.8%	14.5%	12.2%
Tric (ring $^{13}C_{12}$)	99.8%	119.4%	105.4%	111.0%	100.0%	106.7%	7.4%	6.9%	9.1%
BPA (ring $^{13}C_{12}$)	88.5%	87.9%	77.4%	65.5%	88.0%	76.8%	14.6%	19.0%	18.1%
E2 (ring $^{13}C_6$)	105.7%	115.8%	104.2%	109.0%	97.9%	105.7%	6.2%	5.9%	7.7%

Table 9.12: Concentrations (ng L^{-1}) of analytes detected during the three sampling rounds of the 2012/2013 research season, and analyte spike recoveries.

Analyte	Round	Site 1	Site 1 Spike*	Site 2	Site 2 duplicate	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13
mParaben	Round 1	0.8	114.0%	1.0	1.0	<0.8	1.3	0.9	<0.8	0.9	6.2	3.0	2.1	2.7	ND	<0.8
	Round 2	<0.8	177.9%	<0.8	<0.8	<0.8	2.9	<0.8	2.1	ND	30.9	2.8	2.2	37.4	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
eParaben	Round 1	ND	96.7%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	138.3%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
OP	Round 1	ND	120.4%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	428.9%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
pParaben	Round 1	ND	122.5%	<0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	130.6%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
bParaben	Round 1	ND	122.4%	ND	ND	0.5	<0.5	ND	ND	0.7	ND	ND	ND	ND	ND	ND
	Round 2	ND	126.0%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
NP	Round 1	ND	65.0%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	76.6%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
4-MBC	Round 1	<3.2	137.9%	<3.2	3.3	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	ND	ND	ND	<3.2	<3.2
	Round 2	<3.2	57.5%	<3.2	3.5	3.2	<3.2	<3.2	ND	<3.2	<3.2	ND	<3.2	ND	<3.2	<3.2
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

BP-3	Round 1	<2.6	172.3%	<2.6	3.2	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6
	Round 2	<2.6	75.0%	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
mTric	Round 1	ND	98.8%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	101.5%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Tric	Round 1	ND	136.1%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	25.6%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
BP-1	Round 1	ND	153.7%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	120.3%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
BPA	Round 1	4.7	0%	5.7	<1.3	1.5	1.7	1.7	2.4	<1.3	<1.3	<1.3	ND	ND	<1.3	7.7
	Round 2	ND	21.8%	1.9	<1.3	ND	ND	2.9	ND	<1.3	ND	ND	ND	ND	1.4	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
OMC	Round 1	2.5	34.9%	2.0	3.7	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9
	Round 2	<1.9	117.0%	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	1.9	<1.9	<1.9	<1.9	ND	ND	<1.9
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
E1	Round 1	ND	121.7%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	148.4%	ND	ND	ND	ND	ND	ND	ND	<7.0	ND	ND	<7.0	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
E2	Round 1	ND	91.7%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	103.6%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
EE2	Round 1	ND	111.0%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	139.4%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
E3	Round 1	ND	92.7%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 2	ND	119.2%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Round 3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

ND = not detected
NA = matrix interferences prevented quantification
* = low level analyte spike (10 µL) for use in peak identification. Low spike level caused varying recoveries.
– = not sampled

Table 9.12 continued: Concentrations (ng L^{-1}) of analytes detected during the three sampling rounds of the 2012/2013 research season, and analyte spike recoveries.

Analyte	Round	Site 14	Site 15	Site 15 duplicate	Site 16	Site 17	Site 18	Site 19	Site 20	Site 21	Site 22	Site 23	Site 23 Spike	Site 24	Site 24 duplicate	Site 24 Spike
mParaben	Round 1	5.6	–	–	–	<0.8	–	–	–	<0.8	<0.8	<0.8	93.5%	<0.8	<0.8	–
	Round 2	11.6	–	–	–	ND	–	–	–	ND	NA	ND	121.4%	ND	ND	–
	Round 3	–	1.7	2.3	1.4	0.9	0.8	<0.8	2.0	<0.8	ND	<0.8	–	0.8	–	89.6%
eParaben	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	86.8%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	106.1%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	89.9%
OP	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	118.1%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	160.0%	ND	ND	–
	Round 3	–	ND	ND	0.4	–	ND	ND	0.9	ND	ND	ND	–	ND	–	120.6%
pParaben	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	92.4%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	104.6%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	98.5%
bParaben	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	78.7%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	89.8%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	88.1%
NP	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	64.1%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	69.6%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	91.6%
4-MBC	Round 1	ND	–	–	–	<3.2	–	–	–	<3.2	<3.2	<3.2	113.4%	ND	<3.2	–
	Round 2	ND	–	–	–	<3.2	–	–	–	<3.2	NA	<3.2	105.7%	<3.2	<3.2	–
	Round 3	–	<3.2	<3.2	5.8	–	<3.2	<3.2	ND	<3.2	<3.2	3.4	–	4.7	–	139.3%
BP-3	Round 1	<2.6	–	–	–	<2.6	–	–	–	<2.6	<2.6	<2.6	99.3%	<2.6	<2.6	–
	Round 2	<2.6	–	–	–	<2.6	–	–	–	3.7	NA	<2.6	111.6%	<2.6	<2.6	–
	Round 3	–	<2.6	<2.6	3.4	–	2.8	<2.6	3.6	<2.6	<2.6	<2.6	–	<2.6	–	144.0%
mTric	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	98.5%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	101.4%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	91.1%
Tric	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	150.1%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	102.5%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	116.6%
BP-1	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	91.6%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	108.7%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	135.2%

BPA	Round 1	<1.3	–	–	–	ND	–	–	–	ND	<1.3	<1.3	88.4%	<1.3	<1.3	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	89.5%	ND	ND	–
	Round 3	–	<1.3	<1.3	ND	–	ND	ND	<1.3	ND	ND	ND	–	<1.3	–	84.4%
OMC	Round 1	<1.9	–	–	–	<1.9	–	–	–	<1.9	<1.9	<1.9	81.5%	<1.9	<1.9	–
	Round 2	ND	–	–	–	<1.9	–	–	–	<1.9	NA	<1.9	91.6%	<1.9	<1.9	–
	Round 3	–	<1.9	<1.9	2.1	–	<1.9	<1.9	<1.9	<1.9	<1.9	4.3	–	<1.9	–	81.7%
E1	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	78.5%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	113.7%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	115.5%
E2	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	85.2%	ND	ND	–
	Round 2	ND	–	–	–	ND	–	–	–	ND	NA	ND	98.6%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	56.6%
EE2	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	90.0%	ND	ND	–
	Round 2	<1.4	–	–	–	ND	–	–	–	ND	NA	ND	125.7%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND		ND	–	83.3%
E3	Round 1	ND	–	–	–	ND	–	–	–	ND	ND	ND	81.6%	ND	ND	–
	Round 2	<2.1	–	–	–	ND	–	–	–	ND	NA	ND	120.6%	ND	ND	–
	Round 3	–	ND	ND	ND	–	ND	ND	ND	ND	ND	ND	–	ND	–	71.9%

ND = not detected
NA = matrix interferences prevented quantification
– = not sampled

Table 9.13: Concentration (ng L^{-1}) of analytes detected in thawed sea ice samples collected during sampling round 2 of the 2012/2013 research season.

Analyte	Site 2	Site 7	Site 14	Site 17	Site 24
mParaben	ND	ND	ND	ND	ND
eParaben	ND	ND	ND	ND	ND
OP	0.5	ND	ND	ND	0.9
pParaben	ND	ND	ND	ND	ND
bParaben	ND	ND	ND	ND	ND
NP	ND	ND	ND	ND	ND
4-MBC	3.5	3.9	<3.2	4.3	<3.2
BP-3	3.1	<2.6	<2.6	3.8	4.2
mTric	ND	ND	ND	ND	ND
Tric	ND	ND	ND	ND	ND

BP-1	ND	ND	ND	ND	ND
BPA	<1.3	ND	<1.3	ND	ND
OMC	2.3	1.9	2.2	4.8	<1.9
E1	ND	<7.0	ND	<7.0	ND
E2	ND	ND	ND	ND	ND
EE2	ND	ND	ND	<1.4	ND
E3	ND	ND	ND	ND	ND

Table 9.14: Concentrations of micropollutants detected in Antarctic clams (Laternula elliptica), sea urchins (Sterichinus neumayeri) and fish (Trematomus bernachii) (ng g^{-1} dry weight), including analyte and surrogate spike recoveries.

Analyte	Clam 1	Clam 2	Clam 3	Clam 4	Clam 5	Clam 5 duplicate	Clam 6	Clam 6 Spike	Clam 7	Urchin
mParaben	<2.1	4.1	4.4	<2.1	5.8	3.3	3.2	66.5%	<2.1	5.7
eParaben	–	–	–	–	–	–	–	71.9%	–	–
OP	–	–	–	–	–	–	–	29.7%	–	–
pParaben	–	4.3	5.3	4.5	4.3	2.1	–	78.6%	–	–
bParaben	–	–	–	–	–	–	–	74.9%	–	–
BP-3	9.2	78.0	108.3	112.0	72.9	78.7	10.9	53.0%	70.2	8.6
BP-1	–	–	–	–	–	–	–	47.9%	–	–
E1	–	–	–	–	–	–	–	81.2%	–	–
E2	5.2	–	10.9	6.1	–	–	–	69.6%	–	–
EE2	–	8.1	23.1	19.5	15.7	21.5	–	86.3%	12.8	–
E3	–	–	–	–	–	–	–	74.4%	–	–
Cstanol	229.6	49.8	88.5	105.1	76.2	129.4	–	84.5%	–	1255.4
mParaben (ring $^{13}C_6$)	72.6%	75.0%	85.0%	72.2%	68.2%	74.1%	58.9%	65.0%	54.7%	75.8%
bParaben (ring $^{13}C_6$)	77.0%	86.4%	83.6%	73.9%	77.7%	74.8%	71.2%	71.5%	86.0%	81.6%
E2 (ring $^{13}C_6$)	73.6%	39.1%	54.5%	64.1%	73.3%	65.3%	62.0%	63.7%	54.6%	86.6%

Table 9.14 continued: Concentrations of micropollutants detected in Antarctic clams (Laternula elliptica) and sea urchins (Sterichinus neumayeri) and fish (Trematomus bernachii) in ng g^{-1} dry weight, and analyte and surrogate spike recoveries.

Analyte	Fish 1	Fish 1 duplicate	Fish 1 Spike	Fish 2	Fish 3	Fish 4	Fish 5	Fish 6	Fish 7	Fish 1 liver	Average	Std dev	%RSD	95% C.I.
mParaben	7.0	5.1	74.0%	6.8	16.2	19.2	18.9	14.0	26.9	2.4	–	–	–	–
eParaben			84.3%	–	–	–	–	–	–	–	–	–	–	–
OP	3.7	1.6	73.9%	2.4	4.4	1.9	3.5	3.7	5.0	–	–	–	–	–
pParaben	–	–	78.7%	–	–	–	–	–	–	–	–	–	–	–
bParaben	–	–	79.6%	–	–	–	–	–	–	–	–	–	–	–
BP-3	9.6	6.7	67.4%	<6.6	14.1	<6.6	<6.6	11.6	9.1	41.0	–	–	–	–
BP-1	–	–	52.2%	–	–	–	–	–	–	–	–	–	–	–
E1	–	–	74.7%	–	–	–	–	–	–	–	–	–	–	–
E2	–	–	86.3%	–	–	–	–	–	–	–	–	–	–	–
EE2	–	–	109.0%	–	–	–	–	–	–	–	–	–	–	–
E3	–	–	54.3%	–	–	–	–	–	–	–	–	–	–	–
Cstanol	–	–	0%	–	–	–	–	–	–	–	–	–	–	–
mParaben (ring $^{13}C_6$)	86.8%	79.6%	80.7%	51.9%	90.8%	76.5%	79.6%	57.4%	81.6%	54.2%	72.0%	11.6%	16.1%	5.4%
bParaben (ring $^{13}C_6$)	72.5%	65.9%	65.6%	58.3%	71.3%	74.1%	70.1%	55.1%	75.6%	41.3%	71.7%	10.8%	15.1%	5.1%
E2 (ring $^{13}C_6$)	69.0%	78.9%	82.8%	60.2%	61.3%	87.4%	71.6%	66.3%	74.9%	43.8%	66.6%	12.8%	19.2%	6.0%